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GASOLINE COMPOSITION AND VEHICLE EXHAUST GAS POLYNUCLEAR AROMATIC CONTENT

George P. Gross

Esso Research and Engineering Company

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ON

GASOLINE COMPOSITION AND VEHICLE EXHAUST GAS POLYNUCLEAR AROMATIC CONTENT

Period Ending July 30, 1972

CRC-APRAC Project No. CAPE-6-68
EPA Contract 68-04-0025

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16. Abstracts The third-year continuing study developed new information on future emission-control systems and on the combined effects of fuel PNA content and engine/exhaust deposits. Both deposit-formation fuels and various emission-test fuels were used in measuring PNA emissions. One standard production model automobile without emission controls, two with engine-modification controls, and two automobiles with experimental advanced emission control systems have been used in the program. All emission measurements were made on the seven-mode cycle with 2:1 hot/cold weighting. Phenol emissions were reduced by 30 percent in a 1970 vehicle but were not reduced in a 1968 vehicle. Both of the two experimental systems (thermal-reactor and dual-catalyst) reduced PNA and phenol emissions by more than 99 percent relative to the uncontrolled vehicle. Fuel PNA was the dominant fuel-composition factor on exhaust PNA from both uncontrolled and emission-controlled vehicles. Fuels with high PNA content caused deposits which were later emitted, resulting in PNA emissions from two to eight times greater than were observed after use of fuels with near-zero PNA content.

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CRC-APRAC PROJECT CAPE-6-68
THIRD ANNUAL REPORT

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1. SUMMARY

Vehicle emission control systems, fuel composition, and fuel-derived engine deposits have been studied as variables affecting the exhaust emissions of eleven species of polynuclear aromatics (PNA) and phenols. This program was the third year continuation of research supported jointly by the Coordinating Research Council, Inc., and the U.S. Environmental Protection Agency.

Effects of Vehicle Emission Control Systems

Current vehicle emission-control systems substantially reduced the emission of PNA and partially reduced phenol emissions. Two experimental (thermal and catalytic) advanced emission control systems almost completely eliminated PNA and phenol emissions.

	Relative Emissions	
Emission-Control System	PNA	Phenol
None	100	100
Engine-modification (1968)	20-30	100
Engine-modification (1970)	20-30	65
RAM Thermal Reactor	1-2	<0.5
Monel/PTX-5 Dual Catalyst	<1	<0.5

Effects of Fuel Composition

The PNA content (four-ring and five-ring aromatics) of gasoline was the dominant fuel-composition variable affecting PNA emission in both uncontrolled and emission-controlled vehicles. This effect of existing fuel PNA was apparent only after engine deposits had formed from use of the fuel.

Fuel PNA content also dominated the accumulation of PNA in engine oil, and emission control systems did not control this accumulation. Engine oil used for 2000 miles under low oil-consumption conditions with a high-PNA fuel (3 ppm benzo(a)pyrene (BaP) and other PNA) accumulated 12-23 ppm BaP. Small increases (0-2 ppm BaP) in oil PNA also occurred with low-PNA, high-aromatic fuels.

Two-ring and three-ring aromatics (naphthalene, anthracene, etc.), present in a low-PNA gasoline as either a high-boiling reformate fraction or as a heavy catalytic naphtha, caused small immediate increases in PNA emission. In extended use of the gasoline, there was no further increase in PNA emission, but small increases in oil PNA occurred.

Phenol emission was proportional to fuel aromatics and independent of other fuel variables.

Effects of Engine Deposits

Deposits accumulated in the use of high-PNA fuels (3 ppm BaP, etc.) caused PNA emissions which were 1.9 to 8.6 times the emissions measured after use of low-PNA (near zero BaP) fuels. Emission levels were greatest with recently-formed deposits and were reduced by subsequent use of low-PNA fuels. A mechanism of PNA storage in deposits and later release is suggested, and further studies are planned. The magnitude of this fuel PNA effect on PNA emission is undefined for operating conditions differing from these tests. Intermediate levels of fuel PNA have not been evaluated. PNA emission was not affected by deposit-fuel lead, with or without phosphorus.

Effects of Engine Malfunction

Mechanical malfunctions resulting in overchoking at start-up caused extremely high emissions of PNA and soot and obscured the effects of fuel properties. Emissions also increased at least temporarily with higher engine temperatures during a failure of the vacuum spark advance system.

Composition and Sampling of Emitted PNA

Certain more-easily oxidized PNA species, including BaP and benz(a)anthracene (BaA), were significantly less abundant in exhaust PNA samples than in fuel samples, when compared to less-reactive species. These compositional differences could imply either differences in the synthesis of different PNA (engine vs. refinery) or differences in the survival of different PNA that were introduced in a high-PNA fuel or synthesized in the engine. The highest PNA emissions occurred with deposits from high-PNA fuels, implicating survival of fuel PNA as the major factor causing the differences.

These composition differences were shown by special tests to be due, in part, to losses of reactive PNA species that occurred after the sample was collected but before the addition of radiotracers at the start of analysis. These losses resulted in emission measurements for BaP and BaA which were low by a factor of about two. The losses do not invalidate the conclusions reached on the effects of controlled test variables, since all PNA species responded similarly to these variables. Loss-reduction techniques for sampling were developed but were not used because they would introduce an inconsistency with earlier data.

2. INTRODUCTION AND OBJECTIVES

This report covers the work performed on the exhaust emission of polynuclear aromatic hydrocarbons (PNA) and phenols under CRC-APRAC Project CAPE-6-68 in the third year of the Project. Government (Environmental Protection Agency) support (33% of total cost) has been previously provided under Contracts CPA-22-69-56 and CPA-70-104 and is currently provided under Contract 68-04-0025.

While the present work extends past work, a time-gap occurred between the end of the second year in February, 1971, and resumption of contract work on May 6, 1971. During this delay period, several PNA/phenol tests were carried out at the expense of Esso Research and Engineering Company. These Esso tests are described here to the extent that they may affect subsequent contract tests or are essential for data interpretation. To some extent, these tests were in line with contract plans; in any case, they were valuable for maintaining test personnel and test capability during the renewal-negotiation period.

The Second Annual Report (1, 1a) (References are given in Appendix A) reported on the directly observable effects of fuel aromatics, fuel PNA, fuel lead, and the presence of a high-boiling naphtha in a low-aromatic base fuel, and on the effects of vehicle emission-control systems. Also, an approximately two-fold difference in PNA emission levels was apparently associated with the composition of engine combustion-chamber deposits. However, the property of the deposits that controlled the PNA emission level was undefined. Either base (hydrocarbon) composition, high lead as against either low lead or zero lead, or a phosphorus additive in one of the deposit fuels could have been the responsible factor. A review of some of the published studies on fuel composition and deposits, although related in some cases to knock, etc., rather than to pollutant emission, suggested the possibility that some aspect of fuel hydrocarbon composition was a definite possibility as the responsible factor for indirect, or deposit-related, effects. In the area of fuel composition, overall aromaticity, the amount of high-boiling aromatics including PNA, and the presence of other high-boiling naphthas were considered promising for study.

The broad objectives of third-year work in Project CAPE-6-68 were listed in EPA Contract 68-04-0025 and are further condensed and summarized in the following.

- Deposit studies, with special reference to lead and/or phosphorus in deposits, but also including non-leaded deposits.
- Studies of experimental low-emission control systems (as to PNA, phenol, CO, NO, and HC) that may be made available to (but not developed by) CAPE-6, and specifically including Esso's thermal reactor system (RAM) and dual-catalyst (Monel + PTX-5) system. A third system, if made available, through the Project Group from an external source, was also to be tested.

- Validation, in a 1970 test vehicle, of the conclusions from 1966 and 1968 test vehicles. Fuel properties, engine deposits, and control-system effects were included.

- More-detailed studies of fuel-composition effects, beyond overall aromaticity and with special reference to higher-boiling hydrocarbons.

- Additional tasks, as specified by the Project Group and Project Officer, and within the limits of available time and funds.

The objectives summarized above include studies of deposits with lead and/or phosphorus, and also include studies of non-leaded deposits. In the area of direct fuel-composition effects, i.e., effects which appear immediately when a fuel is first tested, special reference is directed to the PNA-emission effects of higher-boiling hydrocarbons. As mentioned above, a variety of published studies have indicated that high-boiling fuel components can influence deposits, and past CAPE-6 work had shown a deposit effect on PNA emission. It was thus appropriate for CAPE-6 to consider fuel hydrocarbon composition, including high-boilers, in the context of deposit fuels, as well as emission-test fuels, i.e., as a factor in defining the PNA-emission level that is associated with any given set of engine deposits after extended use of the fuel.

Fuel hydrocarbon composition, in a broad sense, can imply many different fuel characteristics. One practical approach to the deposit-effect aspects of fuel composition centers logically on high-boiling materials and, specifically, on fuel PNA, i.e., on four-ring and five-ring polynuclear aromatics in the fuel. A small-scale survey by Esso Research, which was made available to CAPE-6 and mentioned in the First Annual Report (2) of CAPE-6, found a substantial variation in the PNA content of gasolines, expressed as the content of benzo(a)pyrene (BaP, five-ring) in ppm or in μg./gallon, where 1 ppm is about 2800 μg./ gallon. The maximum observed BaP content was about 8000 μg./gal. (3 ppm), while the analysis of nationwide composite premium and regular-grade gasoline samples showed 0.43 and 0.19 ppm, respectively. The same report also showed that the residue from distilling a catalytic reformate was a rich source of PNA, including BaP.

In previous CAPE-6 work on deposits, effects were sought in terms of "leaded" vs. "low-lead" and "no-lead" deposits. Deposit-fuel PNA was not a controlled variable in the sense that its presence in a deposit-forming fuel might have affected engine deposits and, in turn, the emission of PNA. In fact, the deposit fuels used in the first two years were not inspected for PNA or BaP content before use, although reasonable estimates can be made. Two commercial premium fuels were used for deposit formation: one contained lead and phosphorus and is known to have been formulated with a catalytic reformate which had not been re-run (distilled) to remove high-boilers. From this knowledge and from tests of later presumably similar fuels, its BaP content is estimated to have been 2-3 ppm. The other deposit fuel base was lead-free and was used both as-purchased and with lead added at 0.5 g./gallon. Inspections of the second of two shipments that were actually used indicates that this fuel contained only about 0.01 ppm of BaP. This second fuel, whether lead-free or with a low-lead level, gave deposits in two test vehicles with which relatively low emissions of PNA were obtained. These differing emission results between deposits from using two differently-based fuels could thus be attributed to differences in either phosphorus use or lead use (with high lead not equal to low lead) or to base-fuel composition. If fuel composition were involved, fuel PNA content appeared to be a promising aspect of fuel composition for further study, since the two fuels could be reasonably assumed to have differed in PNA content (BaP) by a factor of at least 100. No other fuel-composition differences of this magnitude (except additives) were recognized for these fuels.

The third-year deposit-study program evaluated PNA emissions from deposits formed with fuels differing in lead, phosphorus, and PNA content, with each variable at two levels. The effects of two-ring and three-ring aromatics and of a heavy catalytic naphtha were also examined. The same three test vehicles (1966 Plymouth V8, without emission controls (NC), and 1968 and 1970 EM-controlled Chevrolet V8's) that were used previously continued in use. Two experimental low-emission vehicles (RAM thermal reactor and dual-catalyst (Monel + PTX-5)) were loaned by Esso Research and Engineering Co. for emissions tests under conditions that were comparable with existing data from the 1968 Chevrolet (basic vehicle for RAM) and the 1970 Chevrolet (basic vehicle for the catalyst-equipped vehicle). These experimental vehicles are described in References (3) and (4) in substantially the forms used for the CAPE-6 PNA emissions tests.

The third-year program has also provided information in several areas that were outside of the main program but were nevertheless essential to a correct interpretation of the experimental data:

- Engine-deposit condition, or the amount of previous emission testing since deposit formation, influenced PNA emission results.
- PNA present in fuel accumulated in engine oil during fuel use.
- Engine malfunctions caused significant PNA increases.
- Exhaust PNA samples differed from fuel PNA samples, with exhaust samples relatively deficient in certain more-reactive PNA species.

- More-reactive PNA were partially lost in collecting exhaust samples. These losses (about 50% for BaP, for example) did not explain the exhaust/fuel differences, nor did they invalidate the conclusions on the effects of variables on PNA emission.

The first three items above are introduced where appropriate, while the fourth and fifth items are covered separately in Sections 6 and 7 after the discussion, in Section 5, of the results from the main program.

3. EXPERIMENTAL

3.1 Fuels

The fuels used in the CAPE-6-68 program can be grouped as emission-test fuels, prepared in relatively small quantities for emission tests, and deposit fuels, which were used for deposit accumulation and also for most of the third-year emission testing. Both sets are identified by the code designations given in Table 1.

3.1.1 Emission-Test Fuels

Two sets of emission-test fuels (1969 and 1970) have been used, differing primarily in that the 1969 set included a high-boiling naphtha (mixed heavy catalytic naphtha, polymer, and catalytic C_5's) while the 1970 set did not. (Second-year results had found an emissions difference apparently related to the presence of 16% of this naphtha in the low-aromatic test fuel.) Both the 1969 and 1970 sets included low- (11-12%) and high - (46%) aromatic fuels, and the 1970 set was crossblended for 28% aromatics. At these three aromatics levels, fuel TEL content (0,0.5, and 3 grams Pb/gal.) and PNA content (as BaP, at 0.01 and 2.9 ppm) were varied. Table 1 shows the combinations used, and indicates the use of a PNA additive from the distillation of a catalytic reformate. As prepared, the emission-test fuels were very low in PNA content. Compositions and inspections for these fuels appear in Tables B-1 to B-3 on pages 52-54 of the Second Annual Report (1), while inspections of individual blending components are in Table B-4 on page 56 of the First Annual Report (2). Fuels from the emission-test-fuel sets were used for only one-third of the third-year (this report) emissions tests, primarily to relate an engine-deposit condition under study to some earlier deposit condition where the same test-fuel had been used.

3.1.2 Deposit Fuels

Section 2 of this report introduces the composition of a deposit-formation fuel, and particularly its high-boiling components (PNA, etc.), as a potential major variable in defining the level of PNA emissions in exhaust. The code designations for deposit fuels appear in the lower part of Table 1. These fuels can be grouped in two broad groups with respect to PNA content: (a) near-zero PNA, coded A, A', and the indicated blends in these base fuels (except A' + PNA, used only in an emission test and not for deposits), and (b) high-PNA, i.e., 2-3 ppm BaP, coded B, C3P, D and D3. The designations A, A', B, C, and D indicate different base fuels (aromatics, olefins, volatility, etc., as given in Table 2) but we do not, at this time, recognize any substantial effect of these differences, other than PNA content, in terms of deposit-related PNA emissions. Particular attention is invited to the fact that the substantial differences in deposit-fuel PNA contents are not correlated with the boiling characteristics indicated by the ASTM D86 distillation data in Table 2. The one exception here is in the data on 20% blends of two different heavy catalytic

TABLE 1

CAPE-6-68

FUEL IDENTIFICATION

(1) Coded Emissions-Test Fuels; the 1969 set contains a high-boiling naphtha at 16% in the 12%-aromatic and 2% in the 46%-aromatic fuels.

		Fuel Code Designation				
		11-12% Arom.		Cross-blend	46% Arom.	
PNA(a)	TEL(b)	1969	1970	1970	1969	1970
Low	0		1L00	3000	5HOC(c)	5H00
	0.5			3000.5		
	3	100	1L03	3003	5HO	5H03
High	0	108C				5H80
	3	108	1L83		5H8	5H83

(a) Added, as 384+°F VT still bottoms from catalytic reformate (First Annual Report, page 52), at 22.2 gms/gallon to add 8000 μg BaP/gallon, or 2.9 ppm.

(b) In ccs. of TEL/gallon, as Motor Mix. (1 cc TEL contains 1.06 gms Pb).

(c) A similar fuel, 5LOC, of higher mid-fill volatility, was also used in the 1969 set.

(2) Coded Deposit-Formation Fuels, some of which were also used in PNA emissions tests.

A is a commercial lead-free high-aromatic premium gasoline which is low in PNA content; also used with added lead and phosphorus, as A.5 and A3P. A second batch, A', has been used for blending with certain high-boiling components. The blends are coded A' + PNA, A' + V45, A' + HsCN.

B is a lead-free mid-aromatic premium-grade gasoline with substantial PNA content; it is available semi-commercially for engine and vehicle research only.

C is a commercial-type premium-grade (when leaded) gasoline, either purchased or blended by Esso Research from purchased components; components include non-rerun catalytic reformate, and inspected samples of the gasoline contain substantial PNA. Used with lead and phosphorus, as code C3P, in various batches.

D is a fuel similar to C, with higher reformate content and lower volatility. Limited use, without (D) and with (D3) lead.

Suffix 3 means lead at 2-3 grams Pb/gallon.
.5 means lead at 0.5 grams Pb/gallon.
P means phosphorus at 0.2 theory (for $Pb_3(PO_4)_2$) based on lead, or 0.06 grams/gallon when lead is absent.

TABLE 2

CAPE-6-68

DEPOSIT-FUEL INSPECTIONS

(Commercial fuels may vary seasonally)

	Fuel Code Description							
				C3P			A' + 20%	
	A	A'	B	Typical	Recent	D3	HaCN	HwCN
Reid VP (micro)	11.9	12.3	7.8	11-15	13.3	10.6	10.0	10.3
ASTM D-86 Dist.								
IBP, °F	87	92	99	88	86	97	99	93
°F @ 5% Evap.[(a)]	95	100	122	95	95	116	110	102
10	108	116	138	104	105	126	132	122
20	130	148	164	123	121	145	168	167
30	157	190	188	144	138	165	204	204
40	190	216	208	167	158	186	226	225
50	219	228	222	192	178	208	239	236
60	236	237	233	218	198	226	249	248
70	252	246	245	240	221	245	266	263
80	274	263	264	267	246	269	290	286
90	312	307	306	302	285	307	342	342
95	338	335	329	333	325	343	365	365
FBP, °F	378	376	384	376	374	394	420	406
Recovery/Resid./Loss	97/1.5/1.5	96/1/3	98/1/1	96/1.5/2.5	96/1/3	98/1/1	96/1.5/2.5	96/1.5/2.5
Gravity, Lbs/Gal, 60°F	6.26	6.38	6.26	5.9-6.1	5.95	6.10	6.48	6.46
FIA, % Aromatic	37.4	47.2	32.4	23-26	20.4	27.9	49.7	46.4
% Olefin	2.2	0.5	3.1	11-15	8.3	9.5	5.1	4.6
Sulfur, ppm	60	50	<100	100	100	80	—	--
Lead, g/gal	0.0	0.0	0.0	2-2.5	2.1	2.4	0.0	0.0
Phosphorus, Theories	0.0	0.0	0.0	0.2	0.2	0.0	0.0	0.0
PNA, ppm[(b)] BaP	0.01	0.02	2.9	2.2	3.0	3.2	0.07	0.02
BaA	0.01	0.02	2.8	2.5	4.6	3.7	0.08	0.02
BeP	0.01	0.02	2.2	1.8	3.9	2.5	0.07	0.02
BghiP	0.02	0.02	3.4	1.8	5.0	3.7	0.07	0.02
Pyrene	0.09	0.25	7.5	6.0	14.7	8.5	0.37	0.20

(a) Graphical procedure.

(b) ppm calculated from 2800 μg/gal = 1 ppm. See also Table 3. The PNA contents of the 20% heavy naphtha blends were calculated from the component analyses.

naphthas that are included in the table. The naphtha blend having the higher final boiling point does differ in PNA from the lower-boiling blend; this is related to the PNA contents of the two naphthas (Table 3). The blend with the "winter" (lower-boiling) naphtha was prepared, but has not been used experimentally in view of results with the higher-boiling blend.

The PNA contents of the major deposit fuels, of the two heavy catalytic naphthas, and of selected other fuels are given in greater detail in Table 3.

The two heavy catalytic naphthas, mentioned above and examined in the third-year work, are compared in Table 4 with a different high-boiling naphtha (mixed heavy catalytic, polymer, and C_5's) that was used in the first-year (1969) emission-test blends. It is clear that the first-year naphtha was similar to the lower-boiling ("winter") naphtha, rather than to the recently-tested "summer" naphtha. Also, Table B-3 of the Second Annual Report shows by mass spectrometry analyses that the earlier naphtha contributed relatively little additional C_{10}-C_{12} aromatics. This distinction will be mentioned in the Discussion section. The terms "summer" and "winter" applied to the third-year naphthas relate to the practice of some refiners, in some circumstances, to lower the end-point of heavy catalytic naphtha in the winter to produce more heating oil. The implication of this small sample of data, that the end-point of a heavy catalytic naphtha is an indicator of PNA content, should not be generalized without additional data.

3.1.3 Additions of PNA and High-Boiling Aromatics

The test results presented in Section 4 compare the PNA-emission effects of three different additions of high-boiling aromatics to a low-PNA fuel:

(a) Two high-boiling reformate fractions, V4 and V5, from vacuum distillation after prior atmospheric distillation, used in their yield proportions.

(b) The same amounts of V4 and V5, with the yield-proportioned amount of the distillation bottoms, comprising as a whole the "PNA additive" used in this program.

(c) The "summer" heavy catalytic naphtha referred to in the preceding Section. This material contained relatively little PNA.

The use of these three materials increased the high-boiling aromatics present in fuel blends by amounts which are compared in Table 5. Vapor cuts V4 and V5, and the heavy naphtha, increased the amounts of C_{10}-C_{16} aromatics, but did not cause substantial increases in PNA. In the C_{10}-C_{13} range, the use of 20% heavy naphtha caused substantially greater increases than the use of cuts V4 and V5 at the levels at which

TABLE 3

CAPE-6-68

GC/UV ANALYSES OF FUEL PNA (a)

Fuel Sample	PNA Content, μg./gal.								
	Pyrene	BaA	MeBaA	DM/EBaA	BaP	BeP	BghiP	MeBaP	MeBeP
A catalytic reformate	65980	28810	32340	10890	27270	21660	28900	14750	28403
Fuel "D3", with 36% refte.	23670	10340	12260	3990	8970	6940	10260	5730	6190
Fuel "C3P", recent.	41170	12810	6860	1730	8330	10920	14060	2220	2740
Fuel "B", no lead	20890	7810	10320	4020	8060	6260	9490	6117	5940
Fuel "A", no lead	246	28.4	34.5	11.4	26.5	25.5	61.0	17.0	19.4
Fuel "A'",no lead	712	63	40	19	53	55	55	24	24
A "summer" heavy cat. naphtha	2340	920	1030	409	795	798	804	412	520
A "winter" heavy cat. naphtha	26	17	15	4.3	24	20	9.2	1.1	8.7
PNA addition made for a CAPE-6 blend with "high PNA" (b)	32070	6370	5770	2060	8010	6850	9110	4780	4720
CAPE-6 Fuel 108C, using this additive, (anal. in 1970)	30930	6460	7510	2220	8060	7200	11270	5060	5300
Fuel "A' + PNA", using this additive.	33190	6260	6770	2200	10560 (c)	9270 (c)	10270	4760	5520

(a) Chrysene and triphenylene are not available for fuels because of interferences present in the GC peak.

(b) Based on analysis of the additive, and the amount used (22 grams/gallon).

(c) Detailed study of analytical data reveals no basis for rejecting these unexpectedly high values.

TABLE 4

CAPE-6-68

COMPARISON OF HEAVY NAPHTHAS

	First-Year, Mixed HCN/Polymer/ Cat. C_5's(a)	Third-Year Heavy Catalytic Naphthas "Winter"(b)	
		"Winter"(b)	"Summer"(b)
Gravity, lbs./gal., 60°F.	6.38	6.71	6.73
FIA, % Aromatics	37.2	49.8	44.9
% Olefins	29.8	14.5	21.4
RVP, psi	8.6	1.7	2.6
ASTM Dist, IBP, °F	95	139	138
°F at 10% D + L	155	206	208
30%	222	253	260
50%	280	295	305
80%	345	353	375
90%	371	374	402
95%	390	387	420
FBP	419	423	442
% Recovery	97.0	98.0	98.0
% Residue	1.3	1.0	1.5
PNA, µg/gal, BaP	"Zero"(c)	24	795
BaA	"Zero"(c)	17	920

(a) Used at 16 vol % in 12%-aromatic, and 2% in 46%-aromatic emission-test fuels in the first-year test-fuel set. This component was excluded in the second-year set.

(b) Both third-year heavy catalytic naphthas were blended at 20 vol % in base fuel A', but only the "summer" naphtha blend was evaluated in emission tests.

(c) This naphtha was not analyzed directly, but a blend (Code 108C) containing it at 16%, along with a known amount of PNA additive contained only the PNA due to the additive.

TABLE 5

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ADDITIONS OF HIGH-BOILING AROMATICS AND POLYNUCLEAR AROMATICS

	Grams of Aromatics, with Indicated Carbon Numbers, Added/Gallon of Blend[a]		
Aromatic Carbon No.	In 13.3 g of V4 (384-445°F VT) and 6.7 g of V5 (445-575°F VT)	In 22 g PNA Add. (Reft. Fracs. V4, V5, and 575+°FVT Still-Bottoms)	In 20% (v.) of "Summer" Hvy. Cat. Naphtha
10[b]	9.2	9.2	35
11	5.1	5.1	32
12	2.5	2.5	19
13	1.5	1.5	4.7
14	0.8	0.9	0.8
15	0.4	0.9	0.4
16	0.2	0.9	0.2
	19.7	21.0	92.1
PNA Added, µg/gal			
BaP (C_{20})	None[c]	8010	159
BeP (C_{20})	None[c]	6850	160
BaA (C_{18})	None[c]	6370	184
Pyrene (C_{16})	None[c]	32070	468

[a] The C_{10}-C_{16} grams/gallon values are based on LVMS analyses of reformate vapor fractions and bottoms and LVMS and MS analyses of heart-cuts and bottoms from two different distillations of the naphtha. PNA additions (µg/gal) are from Table 3. The computed LVMS results on PNA may be low by 1 carbon number, because, for example, pyrene ($C_{16}H_{10}$ MW 202) is reported as $C_{15}H_{22}$, MW 202.

[b] Includes alkyl benzenes, naphthalene, methylindan, tetralin, etc.

[c] Not analyzed by GC/UV, but the diluted blend does not show PNA absorbance in the UV region for these materials.

they were used. Maintaining these latter levels, but including the distillation bottoms (i.e., using the PNA additive) caused no further change in the C_{10}-C_{13} range but very substantially increased the C_{15+} materials, including four-ring and five-ring PNA. The three cases present different possible real-world situations:

(a) Distillation of catalytic reformate to a high vapor temperature, with bottoms losses minimal.

(b) Use of reformate without distillation.

(c) Use of a high end-point catalytic naphtha (distillation is normal practice, but end-point may vary).

The low voltage mass spectrometer analyses of vacuum distillate cuts from a catalytic reformate, on which part of the foregoing discussion is based, are summarized in Table 6.

3.2 Test Vehicles

The third-year program of CAPE-6-68 continued to use the three standard production vehicles used in the previous work (on loan from Esso Research and Engineering Company), and also made single-test use of two advanced experimental low-emission vehicles that were developed and loaned by Esso Research. In a negotiation period between the second and third contract years, Esso Research used one of the standard vehicles for PNA emission tests, including within the test series a deposit-renewal run on the same fuel used earlier by CAPE-6 and a deposit change through the use of a second deposit fuel. Some of the data obtained in these tests has been made available to CAPE-6.

3.2.1 Standard Vehicles

The standard vehicles used are listed in the following table:

STANDARD TEST VEHICLES

Make	Year	Engine	CID	Emission-Control
Plymouth	1966	V8	318	None
Chevrolet	1968	V8	307	Engine Mod.
Chevrolet	1970	V8	350	Engine Mod.(a)

(a) With transmission-controlled spark retard at low speeds.

TABLE 6

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LOW-VOLTAGE MS ANALYSES OF FRACTIONS FROM A HIGH-SEVERITY CATALYTIC REFORMATE[(a)]

	Total Wt. %, of Aromatics Present in Each Fraction, Having Indicated Carbon Number					
At. Pr. V. Temp., °F.:	358-362	362-372	372-384	384-445	445-575	575 +
Fraction No.:	V-1	V-2	V-3	V-4	V-5	Bottoms
Carbon No.[(b)]						
6	0.21			0.03		
7	2.93	0.94	0.78	0.19	0.10	
8	1.88	1.15	0.74	0.50	0.15	
9	42.58	17.56	5.63	1.88	0.45	
10 (Naphthalene and C_4 Benzenes)	51.99	78.99	88.43	66.97	3.66	0.17
11	0.32	1.32	4.37	27.21	21.53	
12 (Acenaphthene)	0.03			2.88	32.16	
13				0.26	21.36	0.06
14 (Anthracene, Phenanthrene)					12.03	2.07
15					5.59	25.16
16 (Pyrene)					2.34	32.22
17					0.36	18.29
18 (BaA, Chrysene)					0.03	8.77
19						5.91
20 (BaP, BeP)						2.76
21						2.62
22						1.67
Totals	99.94	99.96	99.95	99.92	99.76	99.70
Vol. % of Feed	1.00	0.98	0.99	0.96	0.50	0.12[(c)]
				Mixed for "PNA Additive".		

(a) Fractions by vacuum distillation of 5% bottoms from previous atmospheric distillation. Indicated vapor temperatures are atmospheric equivalents of temperatures observed at reduced pressures. Fractions are essentially 100% aromatic.

(b) Reported carbon no. may be low by 1, or 2, if implied hydrogen is high by 12, or 24. Thus, $C_{24}H_{14}$ will be reported as $C_{22}H_{38}$, and will inflate C_{22}%. Each carbon no. is n in C_nH_{2n-x}, where x may = 6, 8, 10, 12, 14, 16, and 18.

(c) May be low due to recovery losses.

Deposits were created, or changed, in each vehicle prior to a group of one or more PNA emission tests by light-duty cyclic operation on a Mileage-Accumulation Dynamometer (MAD), using a mixed city/suburb/highway regime at an average speed of 30 MPH, and ending in approximately 20 miles of fixed-speed highway operation. Weighed oil changes (Commercial 10W-40, Type SE) and oil filters, and the weights of oil drains and used filters, were used to obtain oil-consumption data in each MAD-operation period. On the MAD, oil-drain intervals of 2000 miles were normally used. Several of the drain-oil samples have been analyzed for PNA content and are reported in Section 4. Begeman (5) has reported that high oil-consumption leads to high PNA emission, and that PNA accumulates in used oils. Table 7 summarizes the deposit-fuel (codes in Table 1), MAD-miles, and oil-consumption histories for the three vehicles since project inception. With the exception of some data involving oil leaks, the oil consumption has remained below 0.5 qts./1000 miles in all vehicles and shows no tendency to increase.

After MAD operation and removal of the used oil and filter, a fresh oil charge and oil filter were installed before each emission test, even if several successive tests were carried out before returning to the MAD. The vehicles were periodically checked with respect to basic spark timing and idle speed, but carburetor and idle mixture adjustments were specifically avoided unless a clear malfunction made them necessary.

The first emission test after MAD operation involved either "stabilized" or "unstabilized" deposits, depending on whether at least seven 7-mode cycles (as required, for example, to obtain emission data on CO, unburned hydrocarbons, and NO) had been conducted with the exhaust to waste, before collecting the total exhaust in the PNA sample collector.

PNA emission tests consisted of three cold-start 12-cycle blocks using 137-second, 7-mode cycles (20). The test procedure is described in greater detail in Section 3.3. A continuous sidestream sample, cooled, filtered, and passed to non-dispersive infrared analyzers, provided emission data on CO_2, CO, HC, and NO; analyses for O_2, and HC by a flame ionization detector, were also recorded. The infrared readings were, in general, processed by an on-line computer, so that up to three emissions values for gaseous pollutants were obtained in each PNA-emission test. The printed values of corrected (to $CO + CO_2 = 15\%$) concentrations of CO, HC, and NO for each mode and cycle used in calculating the emissions results were averaged over the available (1 to 3) blocks that had been computer-analyzed. These results are tabulated in Appendix B. Although emission standards for the 1970 vehicle normally require calculations to a gram/mile basis, the CAPE-6 data on this vehicle were processed only to the concentration basis in order to permit comparison with the two earlier vehicles. The NO emissions, on which no standards exist, were processed as though they were HC emissions, i.e., reading concentrations in the same seconds and using the same weighting factors.

TABLE 7

CAPE-6-68

DEPOSIT-FUEL AND OIL-CONSUMPTION RECORDS

(Deposit Fuels in Order of Use)

Test Vehicle	Deposit-Fuel Code	Miles on MAD	No. of Oil Charges	Oil Cons., Qts/1000 Mi.
1966 Plym.	C3P(a)	1000	1	0.67 (Leak?)
	A	4000	2	0.46
	C3P	2000	1	0.53
	A.5	4973	2	0.64
	A	5023	2	0.70
	D3(b)	2046	1	0.81
	D3	400	1	No Oil Data, Leak Repaired
	D3(c)	609	1	0.33
	B	4084	2	0.43
	A	2012	1	0.35
	A' + V45	2004	1	0.40
1968 Chev.	C3P	1000	1	1.12 (Leak?)
	A.5	5000	2	0.56
	A	5000	2	0.46
	A(d,e)	600	1	No Oil Data
	B(d)	3821	2	0.34
	B	1018	1	0.52
	A	3000	2	0.33
	A' + HsCN	2000	1	0.24
1970 Chev.	C3P	1170	1	0.32
	C3P	2000	1	0.21
	A3P	4011	2	0.36
	A	4019	2	0.36
	B	2008	1	0.27

(a) Before the first 4 tests (clean chambers), these deposits were removed.

(b) A long idle period followed these deposits; the next 400-mile run updated the deposits.

(c) This run was used to check oil consumption in view of high PNA results in Test 61.

(d) Deposits formed by Esso Research.

(e) This run was carried out to update deposits after a long idle period.

The computer-printed emission results provide data on the ppm HC, ppm NO, and % CO emitted (after weighting) and also on the average correction factors required to force CO + CO_2 to = 15%. The average values of these correction factors for each vehicle, treated as a measure of air-dilution, can provide estimates of the average % O_2 in the exhausts of the vehicles. Also, average % CO values can be obtained for each vehicle, as well as average peak exhaust gas temperatures at the muffler exit (see Appendix B). The averages of % CO, estimated % O_2, and peak temperatures are summarized below for each vehicle, using averages of data from all three years.

VEHICLE EXHAUST CONDITIONS

(Three-Year Averages)

	Avg. % CO (7-Mode Test)	Est. Avg. % O2	Avg. Max. °F., Muffler Exit
1966 Plymouth	1.52	0.98[a]	570
1968 Chevrolet	0.75	1.80	594
1970 Chevrolet	0.64	2.56	703

(a) The two-year Plymouth average % O_2 was 1.20%; all other three-year averages are almost identical to the two-year average values reported in the Second Annual Report.

These measures of exhaust condition are believed to influence the emission of PNA, but complete data on this point are not available, because the variations were not systematically explored. However, the PNA from the 1966 and 1968 vehicles is apparently correlated with % CO, and PNA emissions were corrected (see Section 4), by the use of a first-year equation, to standard CO levels in these two cars. (In this regard, CO is not proposed as a causal factor on PNA, but as a symptom of oxygen deficiency, which, along with temperature, can be expected to affect PNA survival and emission.) As in the past, we note that the CO emitted by the 1966 and 1968 vehicles is abnormally low, so that PNA emissions may also be depressed from normal levels.

3.2.2 Low-Emission Vehicles

The two prototype experimental low-emission vehicles (a RAM thermal reactor and a dual-catalyst system) were developed by Esso Research and Engineering Company.

The RAM system has been described by Lang (3). Briefly, it provides reduced NO_x through the use of rich carburetion and spark-timing control and rapidly, after startup, achieves almost total oxidation of CO and HC by reaction with added air in the high-turbulence toroidal reactors located in the exhaust-manifold positions. The system used by CAPE-6 was installed in a 1968 Chevrolet with a 307 CID, V8 engine matched to the standard 1968 Chevrolet used in the regular CAPE-6-68 program. The deposits present in the RAM vehicle when it was used by CAPE-6 were derived from using a high-PNA, leaded fuel.

The dual-catalyst system has been described, in the form used by CAPE-6-68, by Lunt, Bernstein, Hansel, and Holt (4). Briefly, the system used closely-controlled, slightly-rich carburetion and modified spark-timing to produce exhaust gas from which NO was removed by reaction with CO and/or H_2 over Monel saddles in a first reactor, followed by air addition and a second reactor containing Engelhard PTX-5 platinum-on-ceramic oxidation catalyst for control of CO and HC emissions. The system employed by CAPE-6-68 was installed in a 1970 Chevrolet with a 350 CID, V8 engine matched to the 1970 Chevrolet used regularly by CAPE-6-68. The deposits in the catalyst vehicle, when tested by CAPE-6, had been derived from use of a high-PNA unleaded gasoline.

The following table summarizes the emissions (CO, HC, NO) obtained from both experimental vehicles. The CVS emissions relate to tests by Esso Research with these vehicles, using the 1-bag, 23-minute, CVS test (8). The cyclic-test emissions were obtained on an IR-analyzed sidestream during collection of the PNA-emission samples by CAPE-6-68 in 7-mode cycles, and were computed with the usual (1968 standards) weighting procedures. For these results, the instruments were operating at their lower useful limits throughout most of the test.

EMISSIONS OF EXPERIMENTAL VEHICLES

	CVS, gms./mile			Cyclic Test		
Vehicle	CO	HC	NO_x	% CO	ppm HC	ppm NO
'68-RAM	4.2	0.07	1.9	0.07	3	406
'70-CAT	8	0.4	0.7	0.03	12	130

3.3 Production of Samples

The procedure and equipment for sample production were unchanged from the first year and are fully described in the First Annual Report (2).

Operation of the test vehicle on a Clayton chassis dynamometer in three cold-start blocks of twelve 137-second, 7-mode cycles each covered about 30 miles and used about 2-2.4 gallons (weighed) of fuel. The total exhaust, except a sidestream for infrared gas analysis, was cooled and filtered and the condensed water was recovered. The samples analyzed included the water condensate, the filter media, and the solvent washings of all surfaces from the inlet end of the vehicle muffler to the outlet side of the filter. Most of this surface is on the walls of the 84-tube heat-exchanger. The sidestream scrubber tower on the filtered exit gas was not used after the early part of the first year, because results at that time showed it to be of doubtful value for either PNA or phenols. As in the past, muffler washings were included in each sample. The mufflers used were modified by installing drain plugs and flanged inlet and outlet fittings to facilitate their use and cleaning.

At the conclusion of the production run for a vehicle-emission sample, standard practice was to seal the collector unit overnight before removing the filter media and beginning the recovery of sample material deposited on metal surfaces. Third-year experiments using known specimens of BaP, BaA, and benzo(e)pyrene (BeP) exposed to gases at the filter outlet, and also using analyses of separate samples from different parts of the collector, showed that this procedure (overnight residence) permitted reactions to occur which destroyed part of the reactive PNA (BaP and BaA, for example) selectively, leaving the unreactive species (BeP, etc.) unaffected. Section 7 describes these experiments and discusses their implications. After removal of the sample from the collector, radiotracer BaP and BaA were added before concentration of the sample by distillation to a small volume for analysis; once added, the BaP and BaA tracers took any further losses into account, at least for similarly-reactive species.

3.4 Analysis of Samples

Analytical techniques for phenols were unchanged in the third year from the descriptions in the first-year report (2). The aqueous condensate usually contained over 90% of all the phenols, while the Soxhlet extract of the fiber glass filter media contained no phenols. Although many different phenols are present, the data are reported in terms of phenol, i.e., the parent compound. CRC-APRAC CAPE-12-68 at Esso Research has studied techniques for estimating individual phenols in the sample. The technique developed is reported in the forthcoming final report of Project CAPE-12-68, but no more-complex phenol analyses are presented in this report.

All of the third-year CAPE-6-68 PNA-emission samples, as well as selected fuels and oils, have been analyzed by the GC/UV technique for

PNA developed by CRC-APRAC Project CAPE-12-68. An early, but still valid, description of the procedure was given in Appendix E of the Second Annual Report (1) of Project CAPE-6-68. The forthcoming final report of CAPE-12-68 (6) also describes the method. With the exception of occasional missing values, each analysis provided data on the emission (μg.) or content (μg./gal. or ppm) for eleven PNA species:

Benzo(a)pyrene (BaP)
Benzo(e)pyrene (BeP)
Benzo(ghi)perylene (BghiP)
Benz(a)anthracene (BaA)
Methyl BaA (MBaA)
Dimethyl/Ethyl BaA(DM/EBaA)
Methyl BaP (MBaP)
Methyl BeP (MBeP)
Triphenylene
Chrysene
Pyrene

It will be recognized that certain of these "species" are in fact mixtures of several isomers with varying alkyl-group positions. Future plans call for expanding the analyses to additional species, such as perylene, coronene, and the benzofluoranthenes.

Multiple-species analyses on PNA in fuels were already given in Table 3 of this Section, and Table 16 in Section 4 presents data on used-oil PNA contents. PNA species emitted in exhaust samples are reported in Table 22 in Section 6, which also discusses the between-species ratios in samples from different sources. Early CAPE-6-68 emission samples were analyzed for only BaP and BaA, and these two species continue to provide the basis for evaluating the effects of fuel and vehicle variables on PNA emission.

4. EMISSION RESULTS

A summary of data on all tests for the third contract year is presented in Table 8. This table includes data on observed emission rates of benzo(a)pyrene (BaP), benz(a)anthracene (BaA), and phenols (as phenol) per gallon of test fuel consumed. Fuel consumption, aqueous condensate recovery, ambient weather, and computed federal cycle emissions results (1968-1969 model-year method) are also included(a). Tables B-2 through B-41 in Appendix B present average results from one to three test blocks for each mode in six of the twelve cycles that form a block in a sample-production operation. The extreme right-hand columns of these Appendix B tables present the Federal cycle results that appear in Table 8.

The GC/UV analytical method for PNA analysis developed by CRC-APRAC Project CAPE-12-68 has been used on all samples produced in the contract year. The analysis, in its present form (Second Annual Report, Appendix E), gives data on up to 11 PNA species. However, for both simplicity and consistency with past work, the tests are presented and analyzed in terms of BaP and BaA analyses. Section 6 presents the complete PNA analytical results and discusses the interrelation between various samples (fuels, exhaust samples) from different sources. Multiple-species PNA analyses for fuels were given in Table 3 and appear in Table 16 for used oils.

As noted in Section 2, the 1968 Chevrolet test vehicle had been used for seven PNA-emission tests by Esso Research during the delay period between the second and third contract years. Three of the tests were made with A-fuel deposits (low-PNA, no lead) and four with B-fuel deposits (high-PNA, no lead), which were created by Esso Research in 3800 miles of light-duty operation on the Mileage Accumulation Dynamometer. All emission tests used lead-free test fuels. The vehicle was then used in CAPE-6 testing. Emissions of BaP and BaA from two of the Esso tests (E-4 and E-6) are made available and used in this report where they contribute to the presentation. Eleven-species PNA analyses for all seven Esso tests were included in the between-species ratios that were computer-processed for the presentation in Section 6 on average sample compositions.

4.1 Emission of PNA

Two major points are established by the PNA emission data presented in this section: (1) The emissions of PNA from both the thermal-reactor and dual-catalyst experimental vehicles are extremely low. (2) Engine combustion-chamber deposits and, specifically, the PNA contents of the fuels from which they are formed, are dominant factors in governing PNA emission from a given vehicle. (Only deposit fuels with near-zero and near-maximum PNA contents have been studied, however.) It follows that

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(a)For consistency, results from all three vehicles (1966, 1968, and 1970) are presented on the basis of concentrations (ppm or %). For the 1970 vehicle (4000-lb. class), the factors of 23.8 and 0.0127, respectively, will convert the tabulated % CO and ppm HC to grams/mile.

TABLE 8

CRC-APRAC PROJECT CAPE-6-68 -- THIRD YEAR REPORT
SUMMARY DATA SHEET

Vehicle and Test No.(a)	Deposits(b)		Test Fuel(b)		Obs. Emissions/gal. of Fuel			Fuel Cons., gal.	Aq. Cond., lbs.	Fed. Cycle Emissions(c)			Bar. P., "Hg	Humidity Gr./Lb.
	Code	Stabilized(b)	Code	% Ar-BaP-TEL	BaP, μg	BaA, μg	Phenol, mg.			CO, %	HC(C6)	NO, ppm		
'66 Plym.(NC)														
61	D3	No	3003	28-"0"- 3	362	700	294	1.97	12.16	1.59	380	1603	29.97	65
62	D3	Yes	3000	28-"0"- 0	136	155	321	1.96	11.68	1.47	386	1674	30.15	53
61B	D3(d)	Yes(d)	3003	28-"0"- 3	141	167	317	1.96	11.89	1.58	442	1658	29.93	74
68	D3	Yes	A	38-26 - 0	125	129	446	1.96	11.89	1.49	397	1738	30.25	66
69	D3	Yes	B	32-8K - 0	127	185	431	1.95	13.19	1.66	415	1525	30.10	108
73	D3	Yes	D(e)	28-9K - 0	321(e)	360(e)	310	1.99	12.15	1.46	388	1894	30.62	60
76	B	Yes	B	32-8K - 0	169	223	390	1.91	11.20	1.41	401	2073	30.33	42
77	B	Yes	A	38-26 - 0	305(f)	306(f)	463	1.91	10.95	1.32(f)	404	2081	30.51	40
80	B	Yes	3000	28-"0"- 0	98	99	360	2.04	12.28	1.39	388	1824	30.04	68
81	B	Yes(g)	5H00	46-"0"- 0	155	193	700	1.98	11.27	1.41	319	1940	30.00	70
77B	B	Yes(g)	A	38-26 - 0	115	232	528	1.96	11.29	1.32	377	2057	30.20	63
85	A	No	A	38-26 - 0	98	66	453	2.01	11.54	1.24	348	2055	30.06	64
89(h)	A	Yes	A' + V45	47-53 - 0	176(h)	121(h)	540	1.98	10.98	1.34	276	1918	30.26	69
89B(h)	A	Yes(i)	A' + V45	47-53 - 0	453(h)	217(h)	---	2.01	10.77	1.47	259	1644	29.80	58
93(h)	A	Yes(i)	A + V45	38-26 - 0	105(h)	139(h)	539	2.00	12.41	1.78	313	1170	30.02	84
96	A' + V45	No	A' + V45	47-53-0	100	104	562	1.97	11.58	1.84	336	1252	29.91	83
'68 Chev.(EM)														
64	B(j)	Yes(j)	3000	28-"0"- 0	19	25	323	1.97	12.71	0.69	216	1012	30.13	73
65(k)	B	Yes	5H00	46-"0"- 0	16	30	535	1.31(k)	7.83(k)	0.79	149	1065	30.18	57
71	B	Yes	A	38-26 - 0	7.8	20	465	2.03	12.89	0.68	174	1041	30.23	71
72	B	Yes	B	32-8K - 0	36	105	355	2.05	12.60	0.95	168	994	30.25	66
78	B(l)	Yes(l)	B	32-8K - 0	40	100	330	2.04	11.87	0.80	154	1155	30.54	28
79	B	Yes	A	38-26 - 0	163(m)	144(m)	542	2.10	12.72	0.68	162	1014	30.25	68
82	B	Yes	3000	28-"0"- 0	79	82	337	2.09	12.46	0.83	161	1081	29.88	58
86	A	No	A	38-26 - 0	15	29	443	2.00	12.07	0.67	118	1055	29.96	68
90	A	Yes	A' + HsCN	47-200- 0	27	57	548	1.99	11.25	0.83	116	1153	30.08	55
92	A	Yes(i)	A' + PNA	47-10K- 0	18	54	595	2.07	11.50	0.81	80	1182	30.08	58
94	A' + HsCN	No	A' + HsCN	47-200- 0	26	64	580	2.05	12.04	0.69	145	1236	30.18	64
'70 Chev.(EM)														
66	C3P(n)	Yes(n)	3000	28-"0"- 0	12	27	222	2.35	17.14	0.68	167	713	29.81	117
67	C3P	Yes	5H80	46-8K - 0	14	49	370	2.24	14.58	0.47	100	932	30.17	70
70	C3P	Yes	3003	28-"0"- 0	19	39	213	2.35	16.78	0.85	167	794	29.56	100
74	C3P	Yes	A	38-26 - 0	18	38	268	2.26	15.86	0.65	112	836	30.26	89
75	C3P	Yes	B	32-8K - 0	17	60	210	2.25	14.47	0.54	110	1070	30.36	37
83	C3P(o)	Yes(o)	C3P	20-8K-2.1,P	19	101	154	2.36	14.96	0.54	140	1070	30.33	57
84	C3P(p)	Yes	A	38-26 - 0	40(p)	106(p)	299	2.41	13.99	0.54	96	1027	30.33	53
87	A3P	No	A3P	38-26-2.3,P	12	32	299	2.31	13.77	0.56	75	1087	30.08	69
88	A3P	Yes	A3P	38-26-2.3,P	7.8	22	274	2.32	14.29	0.56	78	1018	30.20	70
91	A	No	A	38-26 - 0	10	34	255	2.38	14.10	0.61	94	1078	29.85	71
95	B	No	B	32-8K - 0	72	167	196	2.48	16.14	0.70	86	970	30.06	83
'68 Chev. (Esso RAM)														
60	C3P	Yes	5H8	46-8K - 3	1.6(q)	6(q)	2.3	2.79	17.29	0.07	3	406	30.05	62
'70 Chev. (Esso Dual Cat.)														
63	B	Yes	5H80	46-8K - 0	1.1	1.5	2	2.54	16.60	0.03	12	130	30.17	75

TABLE 8 (CONTINUED

FOOTNOTES

(a) Listed in order of testing for each vehicle; test numbers with letter B represent repeats of earlier tests for various reasons.

(b) Deposit fuels and test fuels are specified by fuel-code symbols; fuel PNA is in μg. of BaP/gallon; TEL in gms. Pb/gal. Deposits are "not stabilized" if light-duty mileage accumulation (dynamometer), ending in highway mode, immediately preceded the emission test. Deposits are "stabilized" if cyclic-test operation (at least seven 7-mode cycles, exhaust to waste, or one or more 36-cycle emission tests) preceded the listed test but after the last deposit-formation operation. There is evidence of a gradual emission decrease, with testing, even for stabilized deposits, particularly with repeated use of low-PNA fuels over deposits from high-PNA fuels.

(c) Averages from computed results for first 7 cycles of 2 or 3 of 3 12-cycle blocks constituting an emission test.

(d) Prior to Test 61B, operated 600 miles on dynamometer, highway-mode end, and stabilized by 12 cycles to waste, all on fuel D3, to check oil consumption (low).

(e) High PNA emissions may be associated with the use of two successive high-PNA test fuels, giving a cumulative effect. See Sections 4.1.3.2 and 4.1.5.

(f) Overchoking in one of three cold starts may have increased PNA emissions in Test 77, but did not significantly affect average % CO.

(g) Tests 81 and 77B were preceded by cyclic-test operation of vehicle on fuel B, with exhaust to waste, to restore deposits to conditions after Test 76.

(h) Test 89 had one start (of 3) overchoked, very rich; Test 89B had two such starts (of 3); Test 93 (carburetor overhaul) had none, but lower A/F ratio in accelerations caused increased CO and lower NO emissions.

(i) Tests 89B, 92, 93 preceded by 12 cycles to waste on A fuel to eliminate possible effects of preceding tests.

(j) B-fuel deposits created by Esso Research between second- and third-year contracts. Three successive low-PNA fuel tests by Esso were marked by decreasing PNA emissions.

(k) Test limited to two 12-cycle blocks.

(l) B-fuel deposits for Test 72 had 7 prior tests since their light-duty accumulation; new B-fuel deposits, and stabilization, preceded Test 78.

(m) PNA emissions are abnormally high. If valid, a process of deposit scavenging is suggested (see also Test 77 in 1966 Plymouth), but the data have been excluded from emission averages on statistical grounds.

(n) A large number of earlier tests (Second-Year Report) had been conducted on these same deposits.

(o) Fresh C3P deposits, followed by stabilization with C3P fuel, preceded Test 83.

(p) Choke-setting difficulty caused one very-rich start (idle 9-12% CO) of three; effect on PNA emission is unknown.

(q) Engine cranking before ignition in one of three starts may have introduced PNA in the exhaust system and may have increased emission results.

in future very-low-emission vehicles, fuel properties (though not explored in this program) should not be significant. In current vehicles, fuel PNA content easily overshadows all other fuel properties that were examined.

In common with previous practice in this project, the PNA emissions (BaP and BaA) from the 1966 Plymouth and 1968 Chevrolet were corrected to standard levels of CO emission (1.5% CO for the 1966 vehicle and 0.8% for the 1968 vehicle, both by the 7-mode cyclic-test computed results). No similar correction is available, nor apparently valuable, for the 1970 Chevrolet test vehicle. The development of the correction equation and its use are detailed in the First and Second Annual Reports. Table 9 lists the % CO and observed (from Table 8) and corrected BaP and BaA emission rates for the two vehicles in the third contract year. Data for these two vehicles are presented and analyzed in the following sections on the basis of the CO-corrected emission data.

At this point, it is appropriate to note that certain PNA species, including BaP and BaA, appear to have been partially lost by chemical reactions from the emission samples before the addition of radiotracer PNA which would account for such losses. The demonstration and magnitude (on the order of 50% for BaP and BaA) of these losses are covered in Section 7. It is shown that the losses were apparently so reproducible that the PNA species that were partially lost were no more variable than the less-reactive loss-free species. Thus changes in the measured amounts of BaP and BaA emitted when controlled variables were changed appear to be valid measures of the relative effects of the variables and continue to be so used. It must be understood, however, that the losses preclude the assumption that quantitatively correct measures of emissions of BaP and BaA are available for even the small 3-vehicle sample used here.

To explain the importance of engine deposits and, in particular, the PNA content of the fuel used to form deposits, it is necessary to introduce the concept of "deposit stabilization." Deposits were accumulated by vehicle operation on a Mileage Accumulation Dynamometer (MAD) under light-duty (city/suburb/highway cycle, 30 MPH average) conditions, with final operation in a highway-driving, fixed-speed, mode. Thereafter, each emission test included repeated accelerations in 36 7-mode, 137-second, driving cycles with three cold starts. It has been found that if an emission test directly followed the light-duty operation, PNA emissions were very much higher from the "unstabilized" deposits than if even a limited amount of cyclic emission-test operation had occurred. In some cases, as little as seven 7-mode cycles (i.e., a CO/HC emissions test for vehicle-acceptance purposes) appeared to "stabilize" the deposits in the sense of causing the next-following test to have PNA emissions not greatly different from those in subsequent tests. More generally, one 12-cycle block, with the exhaust to waste, was used where stabilization was desired. Alternatively, any test other than the test immediately after deposit formation would be a test with stabilized deposits.

TABLE 9

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CORRECTED(a) PNA DATA FOR 1966 PLYMOUTH AND 1968 CHEVROLET, THIRD YEAR

			PNA Emission, μg./gal.			
			Benzo(a)pyrene		Benz(a)anthracene	
	Test No.	% CO	Observed	Corrected	Observed	Corrected
1966 Plym.	61	1.59	362	335	700	649
	62	1.47	136	140	155	160
	61B	1.58	141	133	167	157
	68	1.49	125	126	129	131
	69	1.66	127	112	185	163
	73	1.46	321	334	360	375
	76	1.41	169	184	223	243
	77(b)	1.32	305	368	306	368
	80	1.39	98	107	99	108
	81	1.41	155	169	193	211
	77B	1.32	115	138	232	278
	85	1.24	98	127	66	85
	89(b)	1.34	176	206	121	142
	89B(b)	1.47	453	466	217	224
	93	1.78	105	84	139	111
	96	1.84	100	76	104	79
1968 Chev.	64	0.69	19	21	25	28
	65	0.79	16	16	30	30
	71	0.68	7.8	8.7	20	22
	72	0.95	36	32	105	93
	78	0.80	40	40	100	100
	79(c)	0.68	163	183	144	161
	82	0.83	79	77	82	80
	86	0.67	15	17	29	33
	90	0.83	27	26	57	56
	92	0.81	18	18	54	54
	94	0.69	26	29	64	71

(a) Corrected by first-year equations to 1.5% CO for 1966 Plymouth and to 0.8% CO for 1968 Chevrolet.

(b) Although included here, certain results may be invalid for reasons such as choke manfunctions at startup, which are not evident in overall CO emission.

(c) Wide deviation (unexplained) of this test from normal vehicle level forces exclusion on statistical grounds from averages related to controlled variables.

In the case of deposits from low-PNA fuels, the distinction between PNA emissions from unstabilized and stabilized deposits was much less, since the emission levels were much lower. Data illustrating deposit-stabilization effects will be presented in later sections.

The existence of stabilization as a factor on PNA emission was an accidental discovery growing out of isolated test experiences and analysis of the records of testing details. Only in the latter part of the third year was its true nature realized and the work conducted accordingly. One early, incorrect, impression was that the highway-mode ending of deposit accumulation would stabilize the deposits. It does not, but this was not obvious when using low-PNA deposit fuels, because the stabilization effect is largely evident with deposits from high-PNA fuels.

Recognition of the deposit stabilization concept leads then to two questions: (1) Does a gradual decrease in PNA emissions occur with repeated tests, particularly when repeatedly using low-PNA test fuels over stabilized deposits from high-PNA deposit fuels? (2) Does fuel PNA used in a test of a high-PNA fuel carry over to affect the next-following test? Four selected series of successive tests over deposits derived from high-PNA fuels, for two of the test vehicles and utilizing data from three project years, are listed in Table 10. The emission-test fuels used are specified as to % aromatics and PNA level, which is adequate for the purposes at hand. Three of the four series start with unstabilized deposits. The importance of this condition in causing high emissions is immediately apparent, regardless of the test-fuel used. The selected series also display some downward trend in emissions with time, although the pattern is broken by changes in test-fuel % aromatics and PNA, so that these variables do influence the results and were so used in earlier data analyses. The possibility of overall decline is particularly evident in the last parts of series I and III in the table, where 28%-aromatics fuels gave high emissions after a high-PNA test fuel, and then unexpectedly low emissions. While not absolutely clear, the data in the table also suggest that some carry-over may occur of PNA from a high-PNA fuel in one test to a following test. Several examples that may reflect this situation are cited in Section 4.1.5.

All of these progressive changes (stabilization, gradual decline, and carry-over of PNA) are consistent with a process of deposition and subsequent emission as the mechanism by which fuel PNA leads to emitted PNA. However, they have some obvious implications as to the caution required in comparing tests that are appreciably separated in time (not sequential) over the "same" deposits.

TABLE 10

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CHANGES IN PNA EMISSION WITH SUCCESSIVE TESTS OF LOW-PNA FUELS

(1966 and 1968 test vehicles, three years, with deposits formed from high-PNA fuels)

					CO-Corrected PNA Emission, μg./gal.			
					Using Low-PNA Test Fuels		Using High-PNA Test Fuels	
Test Vehicle	Series No.	Test No., In Order	% Aromatics In Test Fuel	Fuel Used In Deposit Formation	BaP	BaA	BaP	BaA
1966 (NC)	I	15(a)	46	C3P	360	674		
		16	12		-	-	91	212
		17	12		78	182		
		18	46		-	-	165	276
		19	46		127	258		
		20	46		125	196		
		22	11		50	109		
		23	11		-	-	37	134
		26	28		59	157		
		27	28		78	130		
		28	28		63	86		
	II	61(a)	28	D3	335	649		
		62	28		140	160		
		61B(b)	28		133	157		
		68	38		126	131		
		69	32		-	-	112	163
		73(c)	28		-	-	334(c)	375(c)
1968 (EM)	III	5(d)	46	C3P	32	75		
		6	46		32	63		
		7	12		-	-	27	85
		13	12		25	52		
		14	46		-	-	36	85
		21	46		30	55		
		24	11		10.5	40		
		25	11		-	-	13	75
		29	28		36	75		
		30	28		11	28		
		31	28		8.9	20		
	IV	E-4(a, e)	32	B	-	-	83	248
		E-6(e)	38		48	63		
		64	28		21	28		
		65	46		16	30		
		71	38		8.7	22		
		72	32		-	-	32	93

NOTE: The 1970 vehicle does not display a clear trend toward lower emissions with deposit age, but is sensitive to stabilization and to deposit-fuel PNA content.

(a) Fresh, unstabilized, deposits after light-duty use of indicated fuel; all other tests were with stabilized deposits.

(b) Before Test 61B, additional use of fuel D3 to check oil consumption was followed by deposit stabilization.

(c) High emission in Test 73 may reflect the use of two successive high-PNA test fuels over leaded deposits. See Sections 4.1.3.2 and 4.1.5.

(d) Deposits were stabilized, after accumulation, by CO/HC/NO emission tests before the PNA Test.

(e) Between second-year and third-year contracts, Esso Research conducted 3 tests in this vehicle with A-fuel deposits and 4 with B-fuel deposits. Data on emissions on the first and third B-deposit tests are made available above. Tests E-5, -6, and -7 gave progressively less PNA, using low-PNA test fuels. Test 64 then followed under CAPE-6 resumption.

4.1.1 Effects of Current Emission-Control Systems

The 1968 and 1970 Chevrolet test vehicles, with engine-modification (EM) systems for control of CO and HC emissions, were found in the first two years of the project to emit about 70% less BaP and BaA per gallon of fuel than the uncontrolled (NC) 1966 Plymouth. The conclusions were based on geometric means of emission ratios between paired tests in the vehicles, with test fuels and deposits constant between the members of each test pair. Additional data from the three vehicles are now available, but the new tests available are not well-suited to precisely paired comparisons. A different approach is now used, in which the tests in each vehicle, from all three years were grouped first between the presence of stabilized or unstabilized deposits and then whether these deposits were derived from low-PNA or high-PNA deposit fuels. The emission averages from each group for the EM-controlled vehicles are compared in Table 11 in terms of the % reduction in PNA relative to the group-average emissions in the 1966 (NC) vehicle. The numbers in parentheses indicate the number of EM-vehicle tests averaged for each % reduction shown; most of the data derive from high-PNA stabilized deposits. Tables 13 and 14 in Section 4.1.3.1 list the actual grouped data and group averages used for these %-reduction results. The identities of the emission-test fuels used in the averaged tests, and any other variables, are ignored in averaging and are tacitly assumed to average out as non-essential variables for the purpose at hand, if not under other circumstances.

The prior figure of a 70% reduction by the control systems of both cars now appears to be, at least, valid and possibly conservative. Reductions of 75%-80% for BaP and 70-75% for BaA are indicated in Table 11 for both vehicles, particularly for the stabilized-deposit situations from which most of the data are derived.

4.1.2 Effects of Experimental Low-Emission Systems

An order-of-magnitude further reduction in PNA emission was achieved by both of the experimental future low-emission control systems (vehicles 1968-RAM and 1970-CAT) loaned by Esso Research. Evaluations with fuels having high aromatic and high PNA contents, and the presence of deposits from high-PNA fuels, offered the maximum opportunity for high PNA emissions, yet the data given in Table 12 show that the emissions from the experimental vehicles were no more than 1 or 2% of the maximum values seen in the 1966 Plymouth. In fact, these emissions were lower than any observed with any other fuel-vehicle combination in the entire program. Figure 1 shows the data in Table 12 in graphic form. According to data (Section 6) on other PNA species than BaP and BaA in the RAM-vehicle exhaust, this system may be less effective in controlling

TABLE 11

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PNA-EMISSION REDUCTIONS BY EMISSION-CONTROL SYSTEMS

Engine Deposit Condition	PNA Level In Deposit Fuel [(b)]	% Reduction in average PNA Emissions/gal. of fuel for EM controlled vehicles, relative to 1966 NC[(a)]			
		Benzo(a)pyrene		Benz(a)anthracene	
		1968 Chev.	1970 Chev.	1968 Chev.	1970 Chev.
Unstabilized	Low	77(4)	84(2)	53	54
	High	76(1)	79(1)	63	75
Stabilized	Low	73(10)	84(6)	67	76
	High	78(17)	82(19)	69	72

(a) Expressed as the % reduction based on average emissions (for specified deposit descriptions) for the number of emission tests shown in parentheses.

(b) Low-PNA deposit fuels include A, A.5, A3P, A'+V45, and A'+HsCN; high-PNA fuels include C3P, D3, and B.

TABLE 12

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PNA EMISSIONS FROM EXPERIMENTAL LOW-EMISSION VEHICLES

Test Fuel[b] % Ar.-PNA-TEL		BaP and BaA Rates, μg./gallon, in Each Test Vehicle[a] 1966 NC	 1968 EM	 1970 EM	 1968 RAM	 1970 CAT
46-3-0	BaP:	-	-	14	-	1.1
	BaA:	-	-	49	-	1.5
46-3-3	BaP:	165	36	28	1.6	-
	BaA:	276	85	63	6.0	-

(a) When tested, all vehicles had deposits from C3P fuel, except the 1970 catalyst vehicle with B-fuel (no-lead) deposits.

(b) Fuel PNA as BaP in ppm.; TEL in gms. Pb/gal.

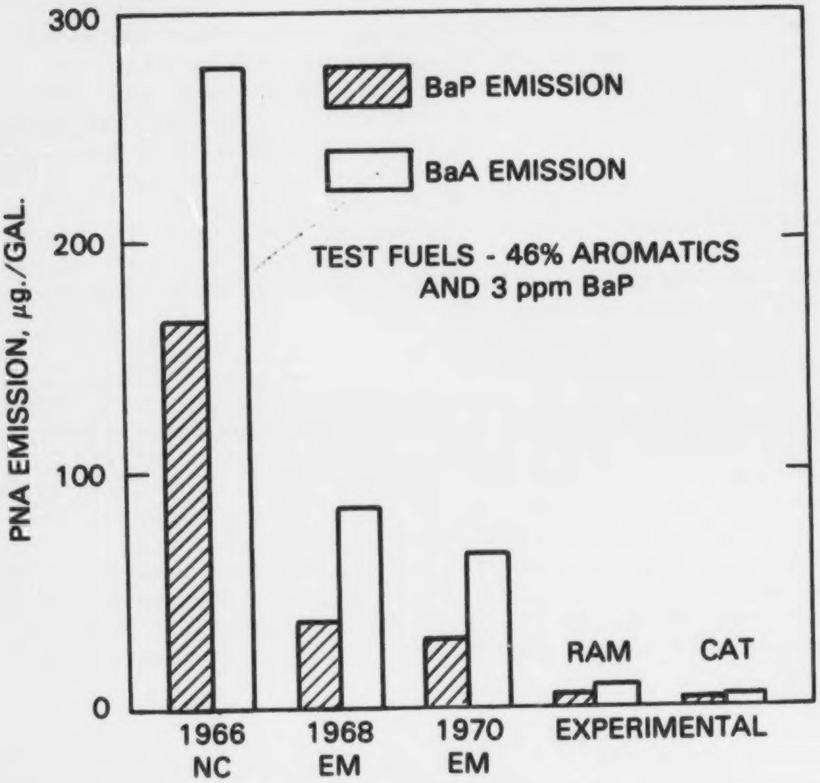

Figure 1

EFFECT OF EMISSION CONTROL SYSTEMS
ON EMISSION OF PNA

less-reactive PNA, such as BeP, than is suggested by the BaP and BaA results. Additional testing would be desirable, however, because existing data may reflect engine cranking that was required for one of the three cold starts.

4.1.3 Effects of PNA in Fuels

The effects of PNA present in fuels can be conveniently separated into effects related to PNA in deposit-formation fuels, effects related to PNA in emission-test fuels, and effects of deposit-fuel PNA on the accumulation of PNA in engine lubricating oil. The studies of fuel PNA have been limited to two levels: near zero PNA and PNA near the field-maximum level determined by Esso Research in a limited New Jersey sampling (2) at the start of Project CAPE-6-68, i.e., that level of PNA characterized by a BaP content of about 3 ppm and which could be introduced by adding 22 grams/gallon of a 384+ °F VT catalytic-reformate still-bottoms containing naphthalene and higher aromatics. The fuels studied for "high PNA" (Section 3.1) were either blended to this level with the still-bottoms additive or already contained approximately this level of PNA.

4.1.3.1 PNA Present in Deposit Fuels

Data showing the importance of some undefined deposit property in establishing a PNA-emission level for a vehicle were presented in the Second Year report. This property caused a roughly two-fold difference in emission levels. The discussion of fuels in the early part of this present report indicates the probability that this property is the PNA-level existing in the fuel used to form the deposits, and this hypothesis appears to be confirmed by recent data. Also, in Section 4.1 the distinction was made between "stabilized" and "unstabilized" deposits, noting that it was particularly significant for deposits formed from high-PNA fuels.

Table 13 lists all the valid BaP and BaA emission data for the three vehicles for the three project years, grouped according to deposit condition (stabilized or unstabilized) and by the identity (code) of the deposit-forming fuel. No distinction is made as to the composition of the emission-test fuel used for each result, even though this does have an effect. Examination of the table readily shows higher PNA emission for (1) unstabilized high-PNA-fuel (C3P, D3, B) deposits compared with stabilized deposits, and (2) for deposits from high-PNA fuels compared with deposits from low-PNA fuels; and reduced PNA emission for the control-system vehicles.

Grouping deposit fuels as low PNA (A, and blends in A or A') or high PNA (C3P, D3, and B) in Table 13 gives the summary in Table 14,

TABLE 13

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PNA EMISSION RESULTS[a] ARRANGED BY CONDITION AND ORIGIN OF ENGINE DEPOSITS

Deposit Condition At Test[c]	Deposit-Formation Fuel	Benzo(a)pyrene, μg./gal.[b]			Benz(a)anthracene, μg./gal.[b]		
		1966 Plym.	1968 Chev.	1970 Chev.	1966 Plym.	1968 Chev.	1970 Chev.
Unstabilized	A	54	15	10	94	17	34
		127	17	-	85	33	-
	A.5	18	3.5	-	30	13	-
	A3P	-	-	12	-	-	32
	A'+VA5	76	-	-	79	-	-
	A'+NaCN	-	29	-	-	71	-
	C3P	360	-	-	674	-	-
	D3	335	-	-	649	-	-
	B	-	83[d]	72	-	248[d]	167
Stabilized	A	56	12	-	126	25	-
		39	12	-	82	23	-
		54	26	-	124	56	-
		56	18	-	155	54	-
		39	-	-	51	-	-
		57	-	-	82	-	-
		62	-	-	104	-	-
		84	-	-	111	-	-
	A.5	36	14	-	49	15	-
		29	3.4	-	46	15	-
	A3P	-	-	7.8	-	-	22
	C3P	91	32	20	212	75	70
		78	32	10.5	182	63	38
		165	27	12	276	85	28
		127	25	29	258	52	52
		125	36	17	196	85	42
		50	30	19	109	55	57
		37	10.5	34	134	40	72
		59	13	26	157	75	60
		78	36	26	130	75	51
		63	11	36	86	28	61
		-	8.9	48	-	20	70
		-	-	20	-	-	31
		-	-	28	-	-	63
		-	-	12	-	-	27
		-	-	14	-	-	49
		-	-	19	-	-	39
		-	-	18	-	-	38
		-	-	17	-	-	60
		-	-	19	-	-	101
	D3	140	-	-	160	-	-
		133	-	-	157	-	-
		126	-	-	131	-	-
		112	-	-	163	-	-
		334	-	-	375	-	-
	B	184	21	-	243	28	-
		107	16	-	108	30	-
		169	8.7	-	211	22	-
		138	32	-	278	93	-
		-	40	-	-	100	-
		-	77	-	-	80	-

(a) A variety of emission-test fuels, not differentiated in this table, were used for the tests listed.

(b) Emissions for 1966 and 1968 vehicles are corrected to uniform CO levels.

(c) Fresh deposits, after light-duty mileage-accumulation, are "unstabilized". Deposits are "stabilized" if operation in at least seven 7-mode 137-second cycles has preceded the listed PNA emission test.

(d) Test result made available by Esso Research from between-contract use of this vehicle, including deposit formation (B fuel) and four emission tests.

TABLE 14

CAPE-6-68

CHANGE IN AVERAGE PNA EMISSION WITH DEPOSIT CONDITION AND PNA CONTENT OF DEPOSIT-FORMATION FUELS

Deposit Condition	Deposit-Fuel Group[a]	Avg. Benzo(a)pyrene, μg./gal.[b]			Avg. Benz(a)anthracene, μg./gal.		
		'66 Plym.	'68 Chev.	'70 Chev.	'66 Plym.	'68 Chev.	'70 Chev.
Unstabilized	Low PNA	69(4)	16(4)	11(2)	72	34	33
	High PNA	348(2)	83(1)	72(1)	662	248	167
	High/Low	5.0	5.2	6.5	8.6	7.3	5.1
Stabilized	Low PNA	51(10)	14(6)	8(1)	93	31	22
	High PNA	122(19)	27(17)	22(19)	188	59	53
	High/Low	2.4	1.9	2.8	2.0	1.9	2.4

(a) Fuels A, A.5, A3P, A'+V45, and A'+HsCN are classed as low in PNA content; fuels C3P, D3, and B are high in PNA content.

(b) Each value listed for BaP emission, with the corresponding BaA value, is the average of the number of results shown in parentheses, as observed with a variety of emission-test fuels.

where the effects of deposits, of deposit-fuel PNA, and of vehicle controls are evident. These emission averages have already been used to calculate the reductions in PNA for control-system vehicles (Table 11). Table 14 includes the ratios of emissions for deposits from high-PNA fuels to those from low-PNA fuels. The ratios demonstrate the highly significant conclusion that deposit accumulation from high-PNA fuels (near the field maximum, or 3 ppm BaP content) causes PNA emissions that are 2 to 9 times greater than for deposits from low-PNA (near zero) fuels. The factors range from 5.0 to 8.6 for unstabilized deposits (emissions in accelerations after light-duty operation) down to 1.9 to 2.8 for stabilized deposits (i.e., subjected to some prior accelerations before testing). The factors are reasonably consistent between vehicles and present a uniform pattern of higher PNA emission for high-PNA deposits. Where the data are adequate to justify analysis, t-tests show the within-vehicle average PNA emissions for the two levels of deposit-fuel PNA to be non-equal at the 90% to 99.9% confidence levels.

It should be noted that this clear distinction between deposits from low-PNA and high-PNA fuels derives from data in which both the deposit fuels and the emission-test fuels vary over wide limits of composition in terms of aromatics, lead and phosphorus contents, and deposit variations within the general class of "stabilized" are also present. The variability in results introduced by these sources of variance does not overcome the major effect of deposit-fuel PNA content. However, it should also be noted that deposit fuels have not yet been tested with PNA intermediate between the extremes used here.

4.1.3.2 PNA Present in Emission-Test Fuels

In addition to the data presented in the preceding section on the long-term effects of fuel PNA, data are available on short-term effects, i.e., with the PNA in the fuel used (about 2 gallons) for the 30-mile emission test. The evidence that fuel PNA affects exhaust PNA through a deposition → scavenging mechanism raises a question whether so short a test is an adequate measure of fuel PNA effects. The Second Year Report used data from three test-fuel pairs in each of three vehicles to find only a non-significant 8% increase in BaP and a 32% increase in BaA for fuel PNA (as BaP content) increasing from 0 to 3 ppm. The tests in each pair (low- and high-PNA) were generally adjacent in the test sequence so that any effects of gradual deposit changes would have been minimized. All of those tests were conducted with deposits from a high-PNA leaded fuel (C3P) present.

In third-year tests, one additional test pair, each involving the same pair of fuels, is available for each vehicle (Table 15). In these tests, deposit fuels A and B were used in that order as emission-test fuels; they are similar except in PNA content. Data for the 1966 Plymouth also extend to a third fuel, D, which is similar to fuel B and

TABLE 15

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EFFECTS OF FUEL PNA ON PNA EMISSIONS

(In sequential thirty-mile tests; third-year data)

Emission-Test Fuel (Code-% Ar.-PNA-TEL) (b)	PNA Emission, μg./gal.[a]					
	1966 Plymouth Tests 68, 69, 73 Deposits From D3		1968 Chevrolet Tests 71, 72 Deposits From B		1970 Chevrolet Tests 74, 75 Deposits From C3P	
	BaP	BaA	BaP	BaA	BaP	BaA
A-38-.01-0	127	131	8.8	22	18	38
B-32-2.9-0	112	163	32	93	17	60
D-28-3.2-0	334	375	-	-	-	-
Relative Emissions						
B fuel/A fuel, as %	88	124	364	422	95	158
D fuel/A fuel, as %	263	286	-	-	-	-

(a) Emissions for 1966 and 1968 vehicles have been corrected to uniform CO levels.

(b) Fuel PNA is stated as ppm Bap and TEL as gms. Pb/gal.

provides the unique case of two successive tests with high-PNA fuels. Another unique feature of the data is the presence of unleaded deposits in the 1968 Chevrolet.

The data show that in the 1966 and 1970 vehicles with leaded deposits, fuel B (high PNA) caused no increase in BaP and a 24% or 58% increase in BaA. These results are consistent with the earlier results from tests with leaded deposits. The data show much larger increases (164% to 322%) in two situations, however: lead-free high-PNA (B-fuel) deposits, and in the second of two tests with high-PNA fuels over leaded deposits. Apparently, the real, potentially large, effect of fuel PNA became evident in 30 or 60 miles, depending on whether the deposits were leaded or not. It follows that the 2000+ miles we have used for deposits appears more than adequate, but the 30-mile emission test may not be adequate. Of course, this conclusion is relevant only to the planning of suitable tests. The large long-term effect of fuel PNA is clearly the most realistic in terms of vehicle emissions and air quality.

4.1.3.3 Effect of Fuel PNA on PNA in Used Oils

GC/UV analyses for the PNA content of fresh oil and of used oils from 2000-mile deposit accumulation runs on a variety of low-PNA and high-PNA fuels are given in Table 16. It is clear that the high-PNA fuels (B, D3), in any of the vehicles, caused much more PNA to appear in the engine oil than was found with the various low-PNA fuels. Even the latter did not entirely avoid the accumulation of PNA compared to the near-zero levels of fresh oil, however. The data on three vehicles using B fuel show that the control (70-80% reduction) in PNA exhaust emissions seen for the 1968 and 1970 (EM) vehicles is not paralleled by any substantial reduction in the buildup of oil PNA.

By way of contrast, it should be noted that in 2000 miles of use of fuels with 3 ppm of BaP, the oil acquires 12 to 23 ppm of BaP. No data are now available on the results with longer oil drains, nor has the effect of this used-oil PNA on PNA emission in the exhaust been determined. All PNA-emission tests have been conducted with a fresh oil charge and new oil filter.

4.1.4 Effects of Lead and Phosphorus in Deposits

Table 17 presents available (3 years) data from sets of emission tests with as nearly as possible the same test-fuel used over different engine deposits at different times in the program. The first set of tests (1966 Plymouth) shows that the results are equivalent for high-PNA leaded deposits, with or without phosphorus. The second set for the Plymouth shows equivalent emissions for 0 and 0.5 grams of lead/gallon in a low-PNA fuel.

TABLE 16

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ANALYSES OF PNA IN USED OILS

(Each oil charge was used for 2000 miles with the indicated fuel)
(Oil is commercial 10W-40, Type "SE")

Fuel (Code) used with Oil:		Code B			Code D3	Code A	A'+V45	A'+HsCN
Vehicle:	Fresh Oil	'66 Plym.	'68 Chev.	'70 Chev.	'66 Plym.	'70 Chev.	'66 Plym.	'68 Chev.
PNA Content of Oil, ppm[(a)]								
Benzo(a)pyrene	0.7	16	16	12	23	0.7	2.6	2.6
Benz(a)anthracene	0.4	17	16	15	25	2.6	2.6	3.0
Benzo(e)pyrene	0.0	21	21	15	28	-	0.9	3.4
Benzo(ghi)perylene	0.0	7.3	15	10	11	0.4	0.4	0.4
Pyrene	3.3	37	40	40	46	10	11	12
Methyl benz(a)anthracene	0.0	20	20	17	27	0.8	2.6	2.5
DiMe/Et benz(a)anthracene	0.0	2.7	3.8	8.3	2.0	0.04	1.7	1.7
Methyl benzo(a)pyrene	0.0	6.3	13	7.5	4.0	0.3	0.4	0.4
Methyl benzo(e)pyrene	0.0	-	26	8.8	-	0.1	3.8	4.5

(a) Analyses for chrysene, triphenylene, and certain other missing species were prevented by interferences in the UV spectra of trapped GC peaks.

TABLE 17

COMPARISON OF PNA EMISSIONS FROM DEPOSITS WITH VARYING LEAD AND PHOSPHORUS

Test Vehicle	Test No.	Test Fuel	Fuel Used For Deposits, And Deposit Condition	PNA Emission[(a)] µg./gal. BaP	PNA Emission[(a)] µg./gal. BaA
1966 (NC)	15	5HO	C3P, unstabilized	360	674
	61	3003	D3, unstabilized	335	649
	34	3000	A.5, stabilized	36	49
	41	3000	A, stabilized	39	51
1968 (EM)	7	108	C3P, stabilized	26	85
	14	5H8	C3P, stabilized	36	85
	25	1L83	C3P, stabilized	13	75
	-	B (est.)	at 32% Ar., high PNA, C3P deposits	(29)	(83)
	72	B	B, stabilized	32	93
	78	B	B, stabilized	40	100
		Avg. for B Fuel		(36)	(96)
1970 (EM)	87	A3P	A3P, unstabilized	12	32
	91	A	A, unstabilized	10	34

(a) Emissions for the 1966 and 1968 vehicles are corrected to uniform CO levels.

The estimates and averages for the 1968 Chevrolet emissions show similar equivalence for deposits for C3P (lead and phosphorus) and B (no additive) high-PNA fuel deposits. Finally, the 1970 Chevrolet data show that lead and phosphorus have no effect on emissions from low-PNA fuel deposits. In summary, lead and phosphorus in deposits do not appear to influence PNA emission.

4.1.5 Between-Test Carry-Over of Fuel PNA

Data in Section 4.1.3.2 and Table 15 suggest a short-term carry-over effect related to deposits. Leaded deposits appeared to "hold back" fuel PNA in a 30-mile test so that it appeared strongly in the subsequent test if use of a high-PNA fuel continued. The long-term effect would still be an emission increase attributable to fuel PNA. However, the short-term effect is significant because it implies the carry-over of high test-fuel PNA from one test to another test in which the test-fuel PNA might be low. Several examples from Project data suggest that this does occur:

1) In the 1968 Chevrolet, low-PNA-fuel Tests 13 and 21 show smaller BaP decreases than BaA decreases, relative to their respective preceding high-PNA-fuel Tests 7 and 14.

2) In the 1968 Chevrolet, Test 29, low-PNA-fuel, showed increased BaP, but constant BaA, relative to the prior Test 25 (on high-PNA-fuel), while the subsequent Tests 30 and 31 on fuels similar to the Test 29 fuel had much lower PNA emissions.

3) In the 1970 Chevrolet, Test 53 (low-PNA fuel), preceded by a high-PNA fuel, Test 52, had higher emissions than occurred with the similar low-PNA fuel used in Test 49.

4) Similarly, in the 1970 Chevrolet, Test 70, low-PNA fuel, preceded by high-PNA-fuel Test 67, had greater emissions than Test 66 using a fuel similar to the Test 70 fuel.

These examples with leaded deposits suggest caution in viewing test results that may be influenced by PNA carry-over.

The carry-over may apply with unleaded deposits, as well, but there are less data available. The effect may explain the unexpectedly high emissions from A fuel (low PNA) after B fuel (high PNA), with B-fuel deposits, in Tests 78 and 79 in the 1968 Chevrolet. A parallel sequence and set of test results appears for Tests 76 and 77 in the 1966 Plymouth (high A-fuel emission after lower B-fuel emission), but the A-fuel test was characterized by a severe choke malfunction in one cold-start and was not accepted as a fully valid test.

4.1.6 Effects of Test-Fuel Aromatics

Fuel aromatics effects were evaluated in the first two years and there is no basis at this time for new conclusions in this area. Some of the potentially useful new data appear to be influenced by PNA carry-over (see above), or by changes in the potency of deposits as PNA sources, i.e., from depletion of the PNA present in the deposits as a result of its in-test emission.

As an example of PNA-depletion in deposits affecting the apparent effects of fuel aromatics, Table 18 presents data from three consecutive tests in two vehicles with the same lead-free, low-PNA fuels used in both vehicles to provide 28%, 38%, and 46% aromatics. Both vehicles had stabilized B-fuel deposits (no lead, high PNA). In order to "maintain" the deposits, the 1966 Plymouth was operated, between tests, on fuel B, in emission cycles, with the exhaust to waste. The 1968 Chevrolet was not operated between tests and had not, in fact, used a high-PNA fuel since the fourth-preceding test (by Esso Research, between contracts); i.e., its deposit PNA could well have been depleted. The Plymouth data in Table 18 are reasonably in line with the fuel aromatics contents, except for the BaA pattern, and are at a level comparable to first-year emissions with other high-PNA deposits in this vehicle. The 1968 Chevrolet data, however, show no aromatics effects. Instead, a downward trend (PNA depletion) appears (Table 10, Series IV), reaching the level seen earlier in this vehicle for A-fuel (low-PNA) deposits. Thus, in six 30-mile tests using low-PNA fuels, the high-PNA character of the B-fuel deposits in the 1968 Chevrolet had been lost.

4.1.7 Effects of Two-Ring and Three-Ring Aromatics

Two-ring and three-ring aromatics (atmospheric-pressure boiling points of 384-575°F) were blended in unleaded low-PNA fuels A and A' (section 3.1) at the concentrations at which they might occur in a fuel with 3 ppm BaP (five-ring) derived from non-rerun catalytic reformate. The PNA (four-ring and five-ring aromatics) were not present in significant amounts. Fuel-supply limitations forced the use of two different but similar low-PNA base fuels, A and A' with 38% and 47% aromatics, respectively. Two vacuum-distillate reformate cuts, V4 and V5, were used together as the aromatics additive with the designation V45.

Data from three tests related to this variable are summarized in Table 19. Between the base-case test, No. 85, and the direct-effect test, No. 93, two tests occurred with severe choke malfunction at startup; the results of these tests were accordingly rejected. Carburetor and choke overhaul then inadvertently caused slightly richer (higher % CO) operation in the subsequent tests. (Prior to these tests, cyclic operation on A fuel, with exhaust to waste, was used to purge any effects of

TABLE 18

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FUEL AROMATICS EFFECTS WITH VARYING DEPOSIT CONDITIONS

Low-PNA Lead-Free Emission-Test Fuel		Stabilized B-Fuel Deposits in Both Vehicles[a]					
		1966 Plymouth, With B Fuel Used (b) Between Tests			1968 Chevrolet, With No Operation Between Tests		
			µg./gallon[c]			µg./gallon[c]	
Code	% Aromatics	Test No.	BaP	BaA	Test No.	BaP	BaA
3000	28	80	107	108	64	21	28
5H00	46	81	169	211	65	16	30
A	38	77B	138	278	71	8.7	22

(a) Tests were performed in the listed order, without intervening tests.

(b) Operation on B fuel (high PNA, no lead) was under cyclic emission-test conditions, with exhaust to waste.

(c) PNA emissions corrected to uniform CO levels.

TABLE 19

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EFFECT OF TWO-RING AND THREE-RING AROMATICS[(a)] ON PNA EMISSION

(1966 Plymouth)

Test No.	% CO	Emission-Test Fuel and Deposit Condition For Emission Test	PNA Emission, µg./gal.			
			Observed		CO-corrected	
			BaP	BaA	BaP	BaA
85	1.24	A fuel, with unstabilized deposits from A fuel.	98	66	127	85
89, 89B	-	Overchoked, defective tests.	-	-	-	-
93	1.78	A+V45, same A-fuel deposit, with test preceded by cyclic operation on A fuel, exhaust to waste, to eliminate any effects of Tests 89, 89B.	105	139	84	111
96	1.84	A'+V45, with unstabilized deposits from 2000 miles on A'+V45.	100	104	76	79

(a) 13.3 grams of 384°-445°F. and 6.7 grams of 445-575°F. fractions/gallon of low-PNA unleaded fuel. See Section on Fuels.

the defective tests and return to the conditions after Test 85.) The PNA data in Table 19 are presented in both "observed" and "CO-corrected" (to 1.5%) bases to show that the same conclusions are reached on either basis and are not caused by the relatively large corrections for CO differences. The data are characterized by BaA values that are both larger (usual), about equal, and less (rare) than the BaP values, as well as by the differences in % CO.

In spite of these differences, the data for Tests 93 vs. 85 show only a small change in BaP (a real decrease is unlikely from the additive, but might reflect a small -- low-PNA -- deposit stabilization difference); and a modest increase in BaA emission. This result is similar to the earlier direct-effect result for added fuel PNA, where the addition involved V45 as well as the four-ring and five-ring still-bottoms aromatics.

Comparing Tests 96 and 93, with similar CO levels, it is clear that the deposits from using fuel A' + V45 for 2000 miles, even though not stabilized and hence presenting a severe case, did not cause increased emission of either PNA species. (Used-oil PNA content (Table 16) increased only slightly from use of this fuel.) Thus, while the presence in fuel of aromatics with two through five rings usually caused a small direct effect and a large deposit-related (long-term) effect on PNA emission, the presence of only two-ring and three-ring aromatics caused a similar short-term effect but no further effect on extended use to form deposits.

4.1.8 Effects of a Heavy Catalytic Naphtha

The test conducted in the third year included tests in the 1968 Chevrolet of the effect on PNA emission of a 20% blend of a "summer" heavy catalytic naphtha (442°F end-point by ASTM D86 distillation (Code HsCN) in a low-PNA unleaded base fuel (Code A'). As discussed in Section 3.1, the naphtha blend contained significantly more C_{11}-C_{14} aromatics (including two-ring and three-ring aromatics) than would be present in a "high PNA" fuel but contained relatively little PNA (four-ring and five-ring aromatics). Thus the heavy catalytic naphtha studies examined a higher level of two-ring and three-ring aromatics than were used in the 1966 Plymouth tests described above, and also introduced other high-boiling materials such as olefins that may be present in the naphtha.

The data obtained are presented in Table 20. The base-case test (No. 86) was carried out with low-PNA fuel A for both deposits and testing, but the lack of additional fuel A forced use of a new very similar fuel, A', having 47% aromatics (vs. 38% in fuel A). The test sequence included a test (No. 92) in which this fuel base was blended with a 384°F + reformate bottoms sufficient to add 2.9 ppm of BaP. This test permits direct comparison of the effects of fuel PNA and of the summer

TABLE 20

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EFFECT OF A HEAVY CATALYTIC NAPHTHA[(a)] ON PNA EMISSION

(1968 Chevrolet)

Test No.	Test Fuel	Deposit Condition	Corrected µg./gal. BaP	Corrected µg./gal. BaA
86	A	Fresh, from A fuel, not stabilized.	17	33
90	A'+HsCN	Next test, no other operation.	26	56
92	A'+PNA[(b)]	Next test, preceded by 12 cycles to waste on A fuel to return to the condition after Test 86.	18	54
94	A'+HsCN	After 2000 miles on A'+HsCN, not stabilized.	29	71
E-4[(c)]	B	After 2000 miles on fuel B (high PNA), not stabilized.	83	248

(a) 20% blend of 442°F. end-point (summer) heavy catalytic naphtha in fuel A', giving blend A'+HsCN.

(b) 22.2 grams of 384+ °F VT reformate still-bottoms/gallon of Fuel A': the addtion imparts 2.9 ppm of BaP with a variety of C_{10}+ aromatics.

(c) Between-contract test by Esso Research.

heavy catalytic naphtha (HsCN). The naphtha (at 20%) was tested for both its direct effect (Test 90) over existing deposits and its deposit-related effect (Test 94).

Comparison of Tests 92 and 86 shows that the PNA additive caused very little difference in BaP emission and a small increase in BaA emission. This is in line with earlier experience for short-term effects of added PNA. The unstabilized deposits in Test 86 were low-PNA deposits. From earlier data, stabilization of such deposits would have little effect on these values. Also, the change in aromatics from 38 to 47% (fuel A to A') has had little effect, since the difference between Tests 86 and 92 is adequately explained by the PNA additive.

Comparison of Tests 90 and 86 does show an increase in emission attributable to use of the naphtha blend in a short-term test. Some, but not all, of the data on blends of a different heavy naphtha in the Second-Year Report also showed increased emission attributed to that naphtha. Test 94, after 2000 miles use of the A' + HsCN blend and without deposit stabilization (i.e., a severe case) shows emissions elevated only slightly from Test 90, where formation of deposits was not involved and the deposits present were stabilized. It is apparent that the heavy catalytic naphtha caused some immediate increase in PNA emission, but no further substantial increase occurred with further use of the fuel for deposit accumulation. By contrast, in Table 20, when this vehicle was operated on high-PNA fuel B for 2000 miles and tested without stabilization, the BaP and BaA emissions were 83 and 248 μg./gallon, or about three times as great as from the 20% heavy catalytic naphtha blend in Test 94.

4.1.9 Effects of Engine Mechanical Defects

In the course of conducting CAPE-6 emission tests, four tests occurred in which known mechanical defects apparently caused significant increases in PNA emission, to the extent that the tests were not useful for their original purposes. The tests do have value, however, as indicators of the possibility that incorrect engine operation can overcome expected reductions in PNA emissions from control systems or fuel properties.

In Test 50 (1970 Chevrolet), loss of the vacuum spark advance hose connection in the third block of the test suppressed NO formation, strongly oxidized deceleration hydrocarbons, increased fuel consumption, and elevated the peak exhaust temperature at the muffler exit by about 80°F. (The TCS system of this vehicle normally prevents vacuum advance below 23 MPH, so the failure described was only effective above that speed.) The BaP and BaA emission rates of 122 and 110 μg./gal. of fuel, respectively, were 2 to 3 times as large as would be reasonably expected for the test fuel (high-PNA) and vehicle. It is abnormal for BaP to exceed BaA, and strongly suggests the "cooking out" of higher-boiling BaP from engine deposits because of the high cylinder-wall and gas temperatures caused by spark retard. The observed increase in PNA was measured against a background of the preceding two "normal" test blocks, so that the effect of the malfunction was probably much larger, when it occurred, than is apparent from the data on the basis available. The effect might not necessarily continue, however, since the supply of PNA in deposits would be depleted.

Tests 77, 89, and 89B in the 1966 Plymouth were characterized by apparent failure of the vacuum-actuated unloader (or "pull-off") on the automatic choke to open the choke blade correctly when the engine started. This occurred in one of three cold-starts in Tests 77 and 89, and two of three in 89B. Using recorded CO_2 and O_2 analyses, the off-scale CO content of the exhaust in these starts was estimated at 12-14%, accompanied by misfire and high unburned hydrocarbon levels. The CO and HC remained somewhat elevated into the first acceleration, by which time the choke had opened to its thermostatically-controlled setting, and operation became normal. The start-ups had little or no effect on the overall computed CO emissions. On examination, the PNA collector system was unusually sooty after these tests. The PNA emissions, even when corrected to uniform CO levels, were quite high for the test fuels and engine deposits:

PNA EMISSIONS WITH OVERCHOKED STARTUP
(1966 Plymouth)

Test	Test Fuel, and Deposit	µg./gal. BaP	µg./gal. BaA	Choke Operation
77	A, stabilized B-fuel deposit	368	368	1/3 stuck
89	A' + V45, stabilized A-fuel deposit	206	142	1/3 stuck
89B	Same as 89, but preceded by cyclic use of A fuel to eliminate any effect of 89	466	224	2/3 stuck

It is not feasible to define precisely the "normal" values for these tests, i.e., to evaluate precisely the effect of the malfunctions; furthermore, the malfunctions were probably not all equal. The implications of comparing 89B (two starts defective) with 89 (one defective) is 260 µg. of BaP and 82 µg. of BaA/gal. as the effect of one incidence of overchoking. Values this high are not tenable in the other tests, however. In fact, the observed results for Test 77 are directionally consistent with a similar test (No. 79) in a parallel test series in the 1968 Chevrolet, where no malfunction occurred, so that the impact of the Test 77 malfunction actually may have been relatively small. In any case, the malfunctions were relatively brief, so the PNA emissions during the defective startups must have been extremely high to affect the final results of 30-mile tests.

4.2 Phenol Emission

Phenol emissions for the third-year program (Table 8) have been combined with earlier data in new linear regressions of emission (mg./gallon) vs. % aromatics in the test fuel, with separate regressions for each of the three test vehicles. The new regressions are plotted in Figure 2 and are compared in Table 21 with those presented in the Second-Year Report. The new regressions do not differ significantly from the earlier ones, but the errors of estimate are now larger and the % of the variance in the data explained by each regression has decreased slightly. Study of the raw data suggests a slight decrease in phenol yields for all three vehicles at higher aromatics levels had occurred in the third year, but the effect does not correlate with deposit type or any other known variable. No new data were obtained at the 11-12% aromatic level. The dominance of fuel aromatics, and the relatively lower phenol emissions from the 1970 Chevrolet (63 to 66% as much phenol as from the 1966 vehicle, for 20%-50% fuel aromatics), continue to be the significant conclusions in this area from the three standard vehicles.

Both of the experimental low-emission vehicles (thermal reactor and dual catalyst) gave extremely low phenol emissions of 2 mg./gallon when tested on 46%-aromatic fuels. These emissions are on the order of 0.3% to 0.5% of the emissions from the base case vehicles (1968 and 1970 Chevrolets) using the same fuels, so that phenol reductions greater than 99% were achieved by both systems. These results are also shown in Figure 2.

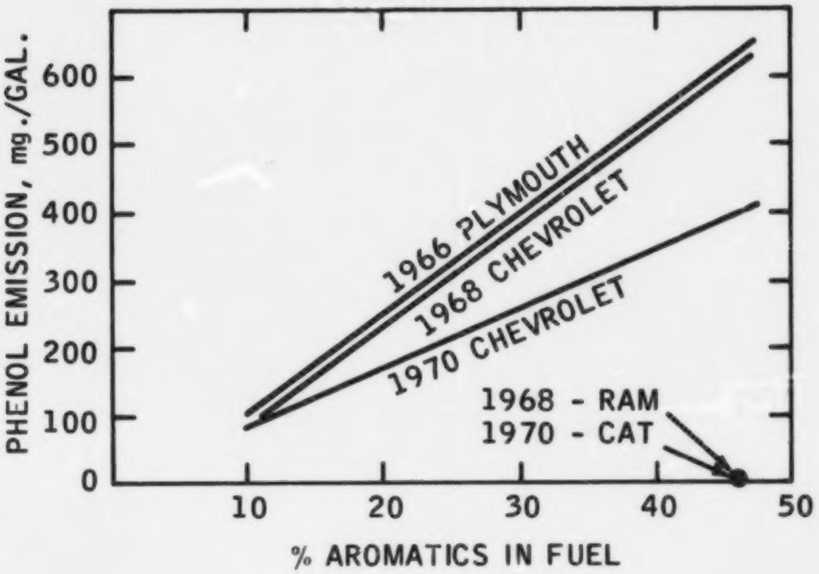


Figure 2

EFFECTS OF FUEL AROMATICS AND EMISSION CONTROL SYSTEMS ON PHENOL EMISSION

TABLE 21

CAPE-6-68

PHENOL-EMISSION CORRELATIONS WITH FUEL AROMATICS

Correlation form: mg./gal. = a + b (% aromatics)

	1966 Plymouth		1968 Chevrolet		1970 Chevrolet	
	2-Year Data	3-Year Data	2-Year Data	3-Year Data	2-Year Data	3-Year Data
Constant, a	-82.0	-40.3	-74.4	-57.1	-15.2	-14.0
Slope, b	17.2	14.5	15.9	14.5	10.1	8.9
Std. error in slope	1.03	0.92	0.58	0.78	0.39	0.61
Correlation coeff.	0.98	0.93	0.99	0.96	0.99	0.95
St. error of est., mg./gal.	53.3	66.8	31.4	49.1	20.8	42.0
% Var. due to Regr.	95.2	87.2	98.0	92.9	98.4	89.5
No. of data Pairs	16(a)	38	17	28	13	27

(a) Several early Plymouth lead-free-deposit tests, then judged to be not at equilibrium were excluded in the second-year correlation, but have been included in the new correlation. Clean-engine (no-deposit) test results (low emissions) were excluded in both correlations.

5. DISCUSSION OF EMISSION RESULTS

The results reported in the foregoing section provide new information in three general areas:

1) the control of PNA and phenol emissions by prototype very-low-emission vehicles;
2) the importance of four-ring and five-ring aromatics (PNA), already present in the fuel as a source of engine deposits which cause relatively high PNA emissions and also as a source of PNA in used engine oil; and
3) the apparently much lower effect on PNA emissions for the presence in fuel of two-ring and three-ring aromatics from high boiling reformate or catalytic naphtha fractions.

5.1 Control-System Effects on PNA Emission

Our previous reports (1,2) and publication (1a) have reviewed the data from CAPE-6-68 and from others showing reductions of about 70-80% in the emission of PNA from vehicles (1968, 1970) having engine-modification emission-control systems, relative to earlier uncontrolled vehicles. Our new data continue to support this level of PNA reduction by these systems. The reductions by EM systems are now shown (Table 11) to occur about equally on a relative basis for PNA emissions from both unstabilized deposits (freshly-formed) and stabilized deposits (subjected to prior cyclic-test accelerations), and for deposits from both high-PNA and low-PNA fuels. This uniformity of control is a highly significant and essential extension of the earlier CAPE-6-68 conclusions, which were based only on stabilized-deposit data, because PNA emissions from unstabilized deposits in 30-mile tests were typically three to four times as great as from stabilized deposits. Since normal driving cycles must include at least some emissions from unstabilized deposits, it is essential to know that current control systems are also effective for this type of emission. Similarly, it is valuable to recognize that the controls are effective with different levels of fuel-derived PNA present in deposits, since marketed gasolines have a wide range of PNA contents.

The data obtained in the dual-catalyst and thermal-reactor test vehicles indicate the probability that the introduction of either type of system for meeting future very-low-emission standards can also achieve very low PNA emission.

For the thermal-reactor (RAM) vehicle, our PNA emissions (1.6 μg. BaP and 6 μg. BaA/gallon of fuel) are somewhat lower than those reported by Hoffman, et. al. (9) for a different reactor system. Hoffman's results on two vehicles (which differed as to BaA emission), when converted to the same units as we have used, are estimated to be around 8 μg. of BaP and either 40 or 130 μg. of BaA/gallon. The difference in PNA emissions of the RAM vehicle and of the system used by Hoffman may be due to warmup differences. Both start-up and later operation are necessarily very rich (high CO) with such systems, so that there is likely to be a very large amount of PNA emitted from the engine cylinders. This PNA must be destroyed in the reactor, where rapid development of high temperatures is essential unless the system is to be, on balance, a high PNA-emitter. The same consideration and differences apply to CO emission. Using the 7-mode cyclic procedure, the RAM vehicle gave a 0.07% CO result, which can be calculated (1970 procedure) as equivalent to about 1.7 grams/mile. (The newer CVS procedures give materially different results.) Hoffman's two 1970 reactor-equipped vehicles were reported to emit 7 and 8 grams of CO/mile, which also suggests that slower warmup may have occurred with these vehicles than with the RAM vehicle.

The dual-catalyst system used by CAPE-6-68 was even more effective than the RAM in eliminating PNA, giving emissions of 1.1 μg. BaP and 1.5 μg. BaA/gallon of fuel. Padrta, et. al. (10) have reported tests with a prototype catalytic-reactor system on a laboratory engine in which over 90% elimination of all PNA species was achieved, with the PNA removal often being greater than the removal of other hydrocarbons. They estimated that an automobile installation would give virtually complete removal of PNA. Griffing (11), however, reported on PNA removal in two catalyst-equipped vehicles where PNA reductions of only 69% and 34% were achieved by the catalysts in hot-cycle tests, and drew the conclusion that PNA reduction by catalysts may be less than HC reduction. We note, however, that Griffing's hot-cycle HC emissions, with the catalysts, were 20 and 79 ppm, while our complete (cold and hot) emission results were only 12 ppm HC. This raises a question whether the Griffing catalysts were sufficiently active to give adequate evaluations of the potentialities for PNA removal in catalytic systems. In any case, one of the Griffing catalyst systems was reported as emitting 50% more PNA in hot cycles than in cold cycles. This result is most unexpected and raises some question of the validity of the Griffing measurements.

5.2 Effects of PNA Present in Fuel

Several reports have been made, by a variety of investigators, on the effects of PNA present in fuels on the emission of PNA. Hoffman (9) found an 87% decrease in BaP emission from a fuel which had been distilled to remove the initial content of 0.7 ppm BaP (and other PNA). Begeman (5) reported that Indolene, with 4 ppm BaP, gave four or five times as much PNA emission as a regular-grade gasoline with 1.1 ppm BaP. Begeman (12) also reported the partial (0.1% to 0.2%) survival and emission of radiotracer BaP that had been added to fuel. Other radioactive PNA species were also emitted, while about 5% of the BaP in the fuel that was used was found to have accumulated in the engine oil, along with other radioactive PNA. Griffing (13) found evidence of a carryover effect of the PNA present in Indolene fuel to a subsequent low-PNA fuel test, causing erratic results. Thereafter, care was taken to avoid this problem by conditioning the test vehicles on low-PNA fuels, and the evaluations of other fuel variables, such as aromatic content or lead, were done on low-PNA fuels exclusively. An earlier single-cylinder study by Griffing (14) had shown increased BaP emission from a high-PNA fuel at several mixture ratios.

In our CAPE-6-68 studies of the directly-observed effects of fuel PNA (3 ppm BaP vs. "0"), we have used isolated, relatively short tests and reported (1, 1a) only nonsignificant (8%) increases in BaP and small (32%) increases in BaA. We continue to find (Table 15) this type of effect for similar tests, but two sequential high-PNA fuel tests, or tests with unleaded deposits present, showed much larger increases in PNA emission from the use of a high-PNA fuel. We have also presented comparisons, in Section 4, of certain sets of our data which show evidence of a PNA-carryover effect and also of the gradual depletion of high-PNA deposits toward a condition of low potential for PNA emission. The extreme examples of this depletion are the observed large decreases in emissions between unstabilized and stabilized deposits from high-PNA fuels.

These experiences in CAPE-6-68 point up the value of the precautions taken by Griffing to avoid PNA carryover and PNA deposits derived from fuel PNA. The Griffing precautions, if taken by CAPE-6-68, would probably have improved the design of our experiments and simplified the interpretation of our data. However, they might also have resulted in the failure to detect the dominant, deposit-related part played by fuel PNA content in determining the exhaust emission of PNA. In view of the short tests used, in which fuel PNA generally did not become fully effective, the effect of fuel PNA would continue to be estimated at the very modest levels which were initially reported. Instead, we now find that, depending on deposit conditions at the time of testing, the presence of PNA (at 3 ppm BaP) in the fuel used for the deposits can cause from 2 to 9 times as much PNA emission as would occur from deposits formed from a "zero"-PNA fuel. This effect can easily obscure the effects of other variables, such as fuel aromaticity, which have received the major attention in most published studies of PNA emission from vehicles or PNA formation in stationary flames and pyrolysis tubes.

It appears, in fact, that fuel aromaticity is practically irrelevant unless fuel PNA is minimized. If fuel PNA were minimized, together with the gradual shift to emission-controlled vehicles, the entire level of automotive PNA emission would be so drastically reduced that aromaticity effects would have little or no practical significance for the atmospheric PNA burden.

The accumulation of PNA in used engine oil is an additional effect of the presence of PNA in fuel. Our results (Table 16) show that the use of fuels with 3 ppm BaP for 2000 miles introduced 12-23 ppm (16 ppm average) BaP in the used oil. Approximating the oil charge at 9 lbs. and the fuel consumed at 900 lbs., we find that 5.3% of the BaP in the fuel has apparently remained in the oil. This is in excellent agreement with the report by Begeman (12) on the use of a fuel with added radiotracer BaP, that "slightly more than 5% of the total amount in the gasoline accumulated in the crankcase oil."

The significance of PNA accumulated in engine oil is not clear at this time. All of the PNA-emission tests by CAPE-6-68 up to the present time have used a fresh oil charge. Future work will evaluate this practice in comparison with leaving the used oil in the engine for the test, and will include cases where the used oil is both high and low in PNA content. The gradual accumulation of PNA in extended oil use (up to 8000 miles) will also be monitored.

The occupational health-hazards related to used engine oils and the disposal practices for used oils appear worthy of examination. The disposal question has been raised recently by Moran (15) in the context of oil incineration.

5.3 Effects of Heavy Reformate and Catalytic Naphtha Fractions

Two-ring and three-ring aromatics (naphthalenes, tetralins, indans, anthracene, phenanthrene, etc.) were evaluated by additions to a low-PNA base fuel in two different ways:

(1) The catalytic reformate vacuum distillate fractions (1.5% of the feed) having atmospheric-pressure vapor temperatures from about 384°F to 575°F were added at 0.7 wt.%. The resulting blend simulated a gasoline made with about 50% of a distilled high-octane catalytic reformate boiling up to 575°F, but containing little or no four-ring and five-ring aromatics.

(2) A heavy catalytic naphtha with an end-point of 442°F (ASTM D-86 distillation) was added at 20% by volume. The choice of naphtha end-point matched the practice of some refiners during periods of lowered heating-oil demand; with higher demand, the naphtha end-point (and C_{10}-C_{14} aromatics content) may be decreased. The use of 20% of the naphtha for blending reflected both the need to maintain a reasonably normal volatility for the blend, 80% of which was an existing low-PNA gasoline, and the fact that marketed gasolines (both premium and regular) may contain from 0 to at least as high as 40% heavy catalytic naphtha. Practical limits are imposed by both octane quality and the legally-specified (in some states) maximum end-point (by D-86) of 437°F.

Adding the reformate-fraction introduced essentially pure aromatics, while the naphtha addition introduced a significantly larger amount of C_{10}-C_{14} aromatics, along with other hydrocarbons such as olefins, indans, and tetralins and also a small amount of four-ring and five-ring (C_{16}+) aromatics (PNA). The presence of PNA in heavy catalytic naphthas can be expected to vary with distillation conditions, such as entrainment of heavy material at high rates of throughput. The ASTM D-86 end-point is not in general a useful guide to PNA content. As pointed out in Section 3, finished gasolines of nearly equal end-points may vary widely in PNA content. Hoffman (9) reported analyses of two heavy catalytic naphthas which contained no BaP or BaA; end-points were not given. In CAPE-6-68 we found (Section 3) that two heavy naphthas differing by about 20° in end-point had about 30-fold to 50-fold differences in BaP and BaA contents, but with the PNA in the higher-boiling naphtha still only about 10% of the level found in various high-PNA gasolines blended from catalytic reformate.

Both methods of addition of two-ring and three-ring aromatics (as reformate fractions and as a heavy catalytic naphtha) were found to have very similar effects on PNA emission. When tested over existing low-PNA engine deposits, both blends gave small increases in BaP and/or BaA emissions. These results suggest that two-ring and three-ring aromatics provide relatively potent starting materials for the synthesis of PNA in an engine. By comparison, much larger increases in single-ring aromatics are required to produce comparable increases in PNA emission. The two blends, when tested over their own, unstabilized (and, hence, of maximum PNA-emission potential) deposits from 2000 miles of operation gave about the same emissions as were seen in the tests from low-PNA deposits, i.e., the accumulation of deposits from these fuel blends did not cause further increases in PNA emission. This is in sharp contrast to the cases in which the deposit-formation fuels were high in PNA content (four-ring and five-ring C_{16}+ aromatics) and much higher PNA emissions were obtained from the unstabilized deposits which they formed.

It is appropriate to discuss briefly the tests reported earlier (1) on the effects of a different high-boiling naphtha on PNA emission. This naphtha (heavy catalytic naphtha + polymer gasoline + C_5's), when used at 16% in a low-aromatic fuel, appeared to cause 40% to 109% more PNA emission than occurred with a similar fuel without the naphtha. This effect was observed only in the 1966 and 1968 vehicles and was actually reversed in the 1970 vehicle. In all cases, the deposits present had been previously formed from a leaded high-PNA fuel. In Section 3.1 of this report, we have indicated that this naphtha contributed no PNA and only a little C_{10}-C_{12} aromatics; its end-point (D-86) was only 419°F. In view of our later results, it is questionable whether it would be likely to have had, at 16%, an increased-emission effect similar to that observed for the 442°F end-point naphtha at 20% which contributed more high-boiling aromatics.

Examination of the sequential test histories for the 1966 and 1968 vehicles shows that the with-naphtha (higher-PNA) tests preceded the without-naphtha (lower-PNA) tests, with several intervening tests all over the same deposits. We now conclude that the apparent effects were due in part to gradual declines in the deposits with successive tests. The reversed effect in the 1970 vehicle also appears to reflect the sequence of testing. We thus conclude that the previously-reported high-boiling naphtha effect may have been, to at least some extent, a spurious effect, even though it was consistent in two of three vehicles with the effect seen later for the higher-boiling heavy catalytic naphtha that contained significantly more heavy aromatics.

5.4 Phenol Emission

The data obtained from the experimental low-emission vehicles indicate that phenol emissions should be essentially eliminated in vehicles which achieve the very low emissions of CO, HC, and NO required in the 1975-76 period. However, existing emission-controlled vehicles (1968 and 1970) continue to show relatively small changes relative to the uncontrolled vehicle (1966) used as a base case (Figure 2, Section 4.2).

The similarity of the phenol emissions from the 1966 and 1968 vehicles, with lower emissions from the 1970 vehicle, may be related to the relatively higher exhaust temperature and/or oxygen content of the exhaust gas from the 1970 vehicle. The temperatures of the 1966- and 1968-vehicle exhausts were more nearly equal. If this distinction is relevant, it implies a fairly uniform phenol production between the three vehicles, but greater destruction in the exhaust system before emission from the 1970 vehicle. The two experimental low-emission vehicles (thermal reactor and catalytic) present the extreme cases of this suggested post-engine oxidation.

5.5 Hydrocarbon (NDIR) Emissions of Vehicles

A review was made of the histories of the three test vehicles with respect to HC(IR) emission over the three project years. First-year and second-year distinctions due to test-fuel aromatic content (affecting instrument response) and to deposit type were less clear in the third-year data, partly because of operation in a narrower range of fuel aromaticity. The previously-reported higher emissions of HC from leaded deposits than from unleaded deposits were no longer evident. However, all emissions of HC in the third year appear to have decreased gradually, and to be incorrect to some extent, because of an undetected progressive change in the shape of the HC(IR) instrument's calibration curve. (Periodic standard samples and span gases were, generally, at the wrong HC levels to detect the change.) Replacement of the IR detector cell and recalibration provided somewhat higher HC emission results in the last three tests of the report period than in recently-preceding tests. However, even after the instrument change, the level remains lower than was common in the first two years.

No correlation of NDIR HC emissions with PNA emissions was found. In fact, an NDIR instrument (hexane-sensitized) responds less to aromatic than paraffinic hydrocarbons, while PNA emissions increase with aromaticity. Thus, no simple correlation could be expected.

6. PNA SAMPLE COMPOSITION STUDIES

6.1 Compositions of Samples of Different Origins

The ratios between various PNA species in samples of different origin have been widely used to characterize the samples, i.e., to develop a "profile" of the sample that is presumably related to its origin. Commins(16) has reported ratio differences for pyrolyses at different temperatures and fuel/air ratios. Oro, et al.(17), have reported ratio differences with temperature in pyrolyzing isoprene, while Cleary(18) has made a similar report on the off-gases from a brick kiln. Badger, et al.(19), reported compositional changes with temperature in the pyrolysis of n-butylbenzene, along with optimum temperatures for the formation of different PNA species.

These papers relate, implicitly, to differences in formation, or synthesis, of PNA with temperature, etc. An inseparable aspect of such studies, however, is the question of relative reactivities of different PNA species for reactions such as oxidation, i.e., the relative extents of survival down to the final analysis, once the individual species are synthesized. (Or, as may be the case in some CAPE-6-68 samples, once the species are introduced into a system (engine), from which they may be emitted at some later time.) Tipson(7) has reviewed the oxidation of PNA, including molecular-orbital calculations of the relative reactivities of several PNA species that are regularly determined in CAPE-6-68 analyses. (Laboratory oxidation studies cited by Tipson support the molecular-orbital predictions.) Tipson's relative reactivities are compared with Badger's optimum-formation (from butylbenzene) temperatures for several CAPE-6-68 species in the following table.

FORMATION TEMPERATURES AND REACTIVITIES FOR SELECTED PNA SPECIES

Compound(a)	Badger's Optimum Formation Temp., °C	Tipson's Relative Reactivity, in Arbitrary Units
Benzo(a)pyrene	710	12
Benz(a)anthracene	660	5
Pyrene	740	3
Phenanthrene	660	1
Benzo(e)pyrene	710	<1
Chrysene	660	0.09
Triphenylene	No Value	10^{-6}
Benzo(ghi)perylene	720	No Value

(a) Phenanthrene is not determined in CAPE-6 samples, but it provides the base case for the reactivity ratings.

It is clear that formation temperatures and reactivities do not correlate. For example, the pairs BaA and chrysene, and BaP and BeP, include widely different reactivities but equal optimum-formation temperatures. Either property might reasonably have some influence on the amount of a given PNA species that is found in an exhaust sample, since both synthesis of PNA from smaller molecules and survival of fuel PNA are involved. Of the two properties, survival rate, or relative reactivity, appears more likely to govern for exhaust samples since the PNA must exit through the hot vehicle exhaust system, with at least some (1% or more) oxygen usually present even before discharge to the air or collection in a cooler-filter unit. If this presumption is correct, we might expect to find progressive changes, between vehicles having different exhaust conditions, in the ratios of, say, the reactive BaP and BaA to their respective, less-reactive isomers, BeP and chrysene. Even larger differences might be expected between the species ratios for fuel samples and those for exhaust samples.

It is necessary to keep in mind, however, a rather severe limitation on all studies of PNA sample composition, or "profiles". The findings of the studies will inevitably reflect any losses of different species in sampling, or differences in analytical accuracy, that may occur after the emission or formation of the PNA sample.

6.2 CAPE-6-68 PNA Sample Compositions

The CAPE-6-68 exhaust samples were collected, with rapid cooling, in a large cooler-filter unit. Washings of unit surfaces and extracts of aqueous condensate and of filter media were combined and known amounts of radiotracer BaP and BaA were added before boildown for analysis. The GC peaks ultimately trapped and assayed by UV absorbance were scaled-up to original values by tracer counting, using BaP* for BaP and BeP (one GC peak) and BaA* for BaA, chrysene, and triphenylene (in another GC peak). The assays of all other peaks were scaled by whichever tracer had the better recovery, i.e., they took the lesser of two alternate values. Almost invariably, BaA*, rather than BaP*, was the tracer used for all species except BaP and BeP.

Two assumptions are implicit: there must be no loss before tracer addition, and all losses after addition must parallel the tracer losses (which includes all factors in the GC analysis that might cause differences in the trapping efficiency or UV-assaying of different GC peaks). In fact, it was generally found from tracer counting that the fraction of BaA* added that was recovered in its GC peak averaged about 28% greater than the fraction of BaP* in its peak. The "correct" choice for scaling other peaks is thus not clear. Furthermore, experiments reported in Section 7 indicate that there probably were losses of some of the more reactive PNA species from, at least, the filter-media portions of the CAPE-6-68 emission samples. However, it will be shown that the ratios of reactive PNA species to non-reactive species are no more variable than the ratios between two non-reactive species. From this it appears that, while losses of reactive species may cause inaccuracies in the absolute PNA emission rates, they should not invalidate conclusions as to the relative effects of changes in controlled variables on these rates.

The question of PNA losses during sampling with equipment such as has been used in CAPE-6-68 has been raised by Griffing(11) in a discussion of Reference (1a). The suggested injection of BaP* (tracer) directly into the exhaust during sampling would require the solution of many technical problems and could, at best, quantify only the emission of BaP. A rigorous measure of the emission of other PNA would still not be available because of the many possible variations in the ultimate recovery efficiency for each species.

6.2.1 Statistical Analysis

In the following presentation, we have analyzed the composition data from CAPE-6-68 emission tests and fuels in terms of between-species ratios to detect significant differences that may be related to the source of the sample. In doing so, we recognize the uncertainty, implied above, whether any given difference is in fact due to the origin of the sample or, rather, to selective losses, before final analysis, that may themselves vary with the origin or later history of the sample.

The data input used for the analysis included:

(1) Eleven-species analyses of emission samples from all accepted (no mechanical defect) CAPE-6-68 tests from No. 32 through No. 96 in the three standard vehicles, and similar data for seven Esso-funded tests in the 1968 Chevrolet. The three vehicles (1966, 1968, 1970) had, respectively, 21, 24, and 27 tests with usable data. Analysis programs were used which could accept the existence of numerous missing values, especially in the lower-numbered tests. The input data appear in Table D-2 of Reference (1) and in Table 22 of this report.

(2) Nine-species (invariably lacking chrysene and triphenylene) analyses on eight fuels from Table 3 of this report and two fuels analyzed ex-contract by Esso Research. Of the fuels listed in Table 3, the first, tenth, and eleventh were excluded as being directly related to other fuels in the table.

A separate analysis was done for the data from each vehicle or from ten fuels, using the following steps:

1. Ratios of BaP, BeP, and BaA, each to ten other species, were computed and converted to common logarithms (base 10).
2. A multiple-regression analysis yielded as general statistics: the mean $\log_{10}$, the standard deviation (s) in the $\log_{10}$, and the actual number (n) of input values (reflecting missing values) for each ratio.

TABLE 22

CAPE-6-68 PNA EMISSION DATA --THIRD YEAR

MULTIPLE-SPECIES ANALYSES OF EXHAUST SAMPLES BY THE GC/UV METHOD OF CAPE-12-68

Test Vehicle	CAPE-6 Test No.	Total Test Yield, µg (for 36 137-Second Cycles)										
		BaP	BeP	BghiP	BaA	Chrysene	Pyrene	Triphenylene	Me-BaA	DM/Et-BaA	MeBaP	Me-BeP
'66 Plym. (NC)	61	712	3672	2217	1377	2998	4382	382	983	468	353	2004
	61B	277	920	916	328	633	3362	124	210	55	63	390
	62	266	1048	1011	304	489	2588	101	246	71	66	526
	68	246	1000	754	254	536	2334	110	203	52	63	442
	69	248	822	1545	360	693	7043	146	289	44	72	367
	73	639	2405	1254	718	1400	4184	215	680	294	186	1260
	76	323	1020	850	427	700	2956	152	324	107	94	506
	77	585	2292	2007	583	1148	6265	306	362	113	155	1017
	80	200	574	606	203	350	1670	93	145	24.4	105	397
	81	308	1110	1414	384	856	4410	179	329	72	102	648
	77B	226	897	942	455	886	3471	146	344	101	61	532
	85	197	624	1075	132	369	2531	90	76	27	79	351
	89	349	1172	1623	240	745	8163	179	59	23	46	230
	89B	911	2659	1886	437	1611	18099	321	81	102	96	308
	93	210	451	786	278	423	5557	100	64	20	23	80
	96	197	484	758	204	395	5853	110	76	26	79	159
'68 Chev. (EM)	64	38	164	240	50	134	615	39	31	8.6	12	69
	65[(a)]	32	127	229	59	126	815	37	25	8.0	7.4	51
	71	16	72	112	40	87	510	35	13	3.3	4.7	21
	72	74	289	349	216	303	1597	72	119	28.7	14	142
	78	81	836	384	203	622	1515	79	112	2.5	0	493
	79	343	1233	488	302	701	953	158	371	192	174	708
	82	165	769	1102	171	297	847	59	137	51	52	526
	86	30	98	239	59	153	896	42	29	5.1	6.2	24
	90	54	164	334	114	282	1256	59	31	8.7	10.5	44
	92	38	156	78	113	218	1454	52	50	6.9	5.6	46
	94	53	193	189	132	222	1237	49	59	14	15	69
'70 Chev. (EM)	66	28	118	163	64	131	466	37	31	6.2	7.7	41
	67	32	177	236	110	241	1330	62	61	14	8.3	64
	70	46	219	277	92	198	814	53	43	9.5	12	72
	74	40	192	324	85	146	719	45	36	12	7.7	61
	75	39	196	184	135	225	1043	52	69	18	9.9	71
	83	44	474	245	239	377	1299	75	83	20	11	86
	84	96	628	611	254	473	1525	94	103	Lost	16	118
	87	27	139	296	74	204	688	52	21	3.7	5.3	27
	88	18	78	155	50	108	620	38	16	4.7	2.9	14
	91	24	121	225	80	181	776	56	24	6.9	5.0	20
	95	177	814	369	413	662	2000	134	355	96	62	477
'68 Chev. (RAM)	60	4.5	82	47	17	(b)	117	(b)	(b)	5.0	2.6	10.7
'70 Chev. (Monel/PTX-5)	63	2.8	5.3	2.8	3.9	5.7	64	2.2	1.6	0.0	0.1	1.5

[(a)] Only 24 cycles were run to conserve fuel, but yields are adjusted to 36-cycle basis.

[(b)] Methyl- and dimethylpyrenes interfered with determinations of several species.

NOTE: Tables 3 (Fuels) and 16 (Oils) present additional GC/UV PNA analyses.

(3) Antilogs of the mean $\log_{10}$ values and of the mean $\log_{10} \pm 2\, s/\sqrt{n}$ were printed as geometric mean ratios and 95% confidence limits on the means, i.e., the upper and lower limits of the mean ratios.

Table 23 presents the geometric mean ratios and 95% confidence limits, as defined in (3) above, and Figures 3 through 5 display the ratios and limits on logarithmic scales.

6.2.2 Reactivity Differences Betweeen PNA Species

In the absence of chrysene and triphenylene data for the fuels, benzo(e)pyrene (BeP) is the least reactive species on which fuels analyses are available. As a result, the most convenient way to examine the PNA ratios to detect reactivity effects is the use of Figure 3, where BeP is common to all ratios. Inspection of the fuels ratios (BeP to other species) in Figure 3, as against the three sets of vehicle ratios, shows that, in fuels, the mean ratios of BeP to BaP, BaA, MeBaA, DM/EtBaA, and MeBaP are all significantly different from their values in the three vehicles. Conversely, ratios of BeP to BghiP, pyrene, and MeBeP are the same in fuels as in the vehicle exhausts, except that, in the 1970 vehicle exhaust, BeP/MeBeP is different from its value in fuels. (This vehicle's exhaust is the hottest and has the highest oxygen content of the three.) The implication here is that the severe conditions of passing through an engine destroys the reactive BaP, BaA and their alkyl derivatives, relative to the less-reactive BeP, MeBeP, pyrene, and BghiP, so that the ratios for reactive species in the exhaust differ from those in the fuels. The magnitudes of changes in geometric mean BeP ratios (Figure 3) from "fuels" to "1970 vehicle" were calculated as the differences between the mean logs of the ratios. These differences were then ranked as measures of reactivity, with the result that the nine available species were ranked in decreasing order of reactivity as follows:

Decreasing Reactivity	Rel. Reactivity (Tipson)
MeBaP	--
DM/EtBaA	--
MeBaA	--
BaP	12
BaA	5
MeBeP	--
Pyrene	3
BghiP	--
BeP	<1

The order derived in this way from the CAPE-6 data exactly matches the order cited by Tipson for four of the species, as calculated from molecular-orbital theory. The alkyl derivatives, as expected from the chemistry of simple aromatic hydrocarbons, are found to be more reactive than the parent compounds.

Table 23

RATIOS BETWEEN PNA SPECIES IN EXHAUST SAMPLES AND IN GASOLINES

(Stated as the geometric means and upper and lower (95%-confidence) limits on the means.)

PNA Analyses from Tests 32+ are included; each mean is derived from at least 14 vehicle-emission samples or 9 fuel analyses.

Ratio of	Samples from 1966 Plymouth (21 Tests)			Samples from 1968 Chevrolet (24 Tests)(a)			Samples from 1970 Chevrolet (27 Tests)			Gasolines and Naphthas (10 Samples)(a,b)		
	Lower	Mean	Upper	Lower	Mean	Upper	Lower	Mean	Upper	Lower	Mean	Upper
BaP/BeP	0.267	0.308	0.356	0.222	0.254	0.290	0.162	0.183	0.207	0.903	1.038	1.193
BghiP	0.251	0.289	0.333	0.179	0.221	0.273	0.176	0.221	0.279	0.662	0.886	1.187
BaA	0.690	0.769	0.857	0.423	0.501	0.592	0.378	0.437	0.504	0.667	0.853	1.089
Chrysene	0.332	0.381	0.438	0.194	0.230	0.274	0.194	0.225	0.261			
Pyrene	0.056	0.071	0.088	0.039	0.054	0.073	0.050	0.064	0.083	0.154	0.244	0.386
Triphenylene	1.519	1.796	2.122	0.663	0.866	1.131	0.705	0.845	1.013			
MeBaA	0.990	1.276	1.645	0.798	0.948	1.126	0.784	0.946	1.140	0.697	0.909	1.185
DM/EBaA	3.335	4.447	5.929	3.065	4.127	5.557	3.110	3.850	4.767	1.997	2.696	3.638
MeBaP	2.776	3.384	4.126	3.085	3.574	4.141	3.753	4.252	4.818	1.626	1.979	2.410
MeBeP	0.489	0.633	0.819	0.452	0.571	0.720	0.495	0.600	0.727	1.593	1.907	2.284
BeP/BaP	2.807	3.239	3.738	3.438	3.932	4.496	4.813	5.450	6.170	0.837	0.962	1.106
BghiP	0.727	0.876	1.055	0.712	0.910	1.163	0.915	1.209	1.597	0.663	0.853	1.099
BaA	2.098	2.501	2.980	1.656	2.014	2.449	2.072	2.382	2.739	0.708	0.821	0.952
Chrysene	1.003	1.227	1.502	0.761	0.922	1.117	1.079	1.230	1.401			
Pyrene	0.164	0.223	0.303	0.154	0.221	0.317	0.281	0.354	0.445	0.159	0.235	0.346
Triphenylene	5.306	6.400	7.720	2.621	3.589	4.915	3.823	4.721	5.830			
MeBaA	3.630	4.355	5.225	3.338	3.953	4.680	4.096	5.155	6.488	0.687	0.875	1.116
DM/EBaA	12.349	15.176	18.650	11.825	17.204	25.081	16.158	20.744	26.633	1.966	2.651	3.575
MeBaP	9.539	11.551	13.986	12.269	14.124	16.259	19.371	23.172	27.720	1.401	1.937	2.678
MeBeP	1.822	2.160	2.561	2.062	2.381	2.749	2.618	3.270	4.083	1.413	1.836	2.386
BaA/BaP	1.166	1.299	1.448	1.686	1.995	2.360	1.980	2.287	2.641	0.917	1.172	1.497
BeP	0.335	0.399	0.476	0.382	0.496	0.643	0.365	0.419	0.482	1.050	1.217	1.411
BghiP	0.310	0.373	0.449	0.347	0.454	0.596	0.398	0.507	0.646	0.806	1.039	1.340
Chrysene	0.457	0.495	0.537	0.427	0.460	0.495	0.487	0.516	0.547			
Pyrene	0.072	0.091	0.114	0.085	0.106	0.132	0.127	0.148	0.173	0.196	0.286	0.417
Triphenylene	1.969	2.286	2.655	1.409	1.729	2.121	1.802	2.044	2.318			
MeBaA	1.268	1.537	1.864	1.570	1.871	2.230	2.002	2.295	2.630	0.897	1.066	1.267
DM/EBaA	4.255	5.358	6.746	5.595	8.143	11.851	7.871	9.291	10.968	2.476	3.184	4.094
MeBaP	3.151	4.078	5.276	5.232	6.954	9.243	8.335	10.316	12.768	1.661	2.454	3.627
MeBeP	0.578	0.762	1.004	0.820	1.127	1.548	1.099	1.456	1.927	1.626	2.236	3.075

(a) A limited amount of ex-contract data for the 1968 Chevrolet and for two gasolines were included.

(b) Chrysene and triphenylene are not available in fuel PNA analyses because of interferences by other compounds.

Figure 3

RATIOS OF BENZO(e)PYRENE TO OTHER PNA IN EXHAUST SAMPLES AND GASOLINES

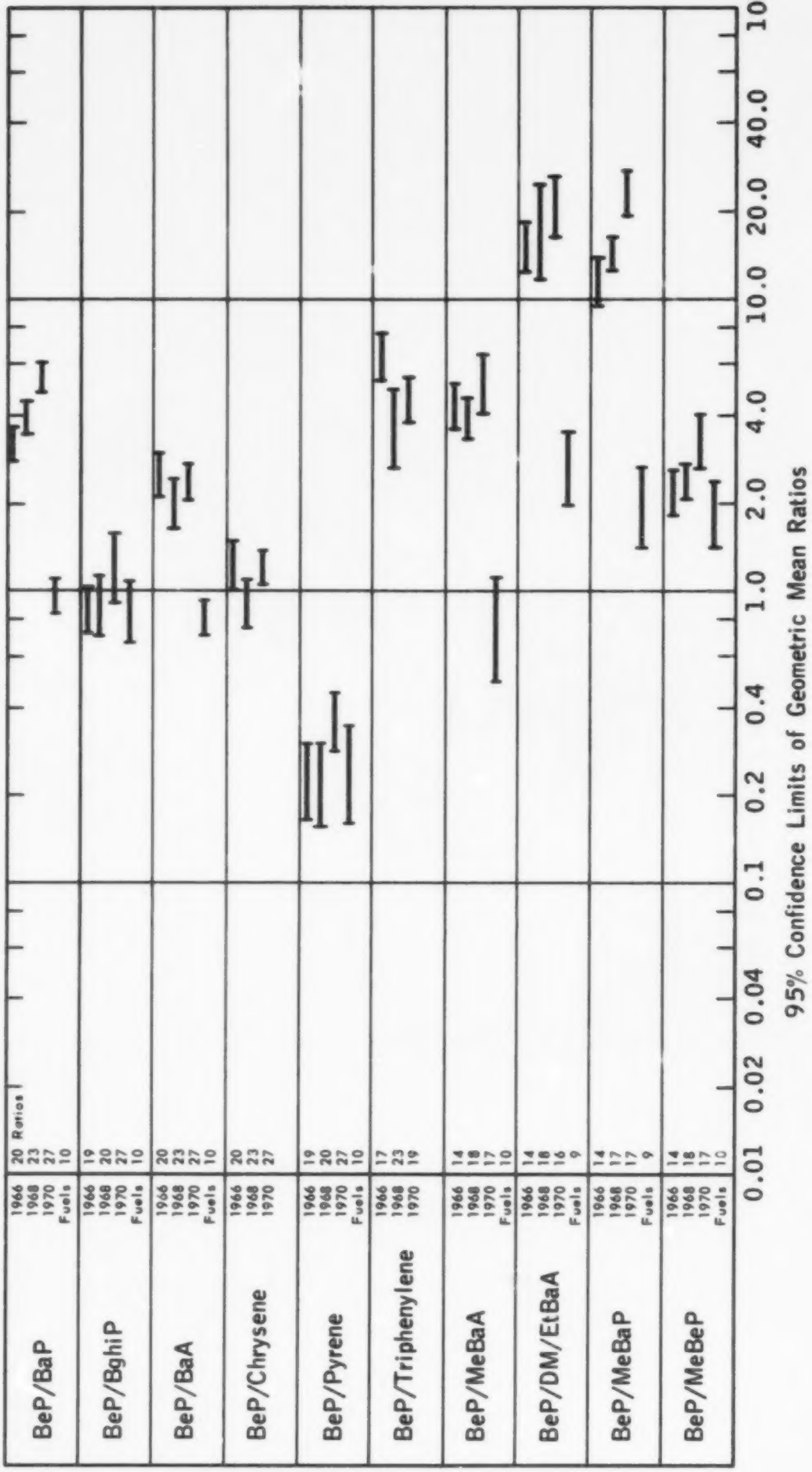


Figure 4

RATIOS OF BENZO(a)PYRENE TO OTHER PNA
IN EXHAUST SAMPLES AND GASOLINES

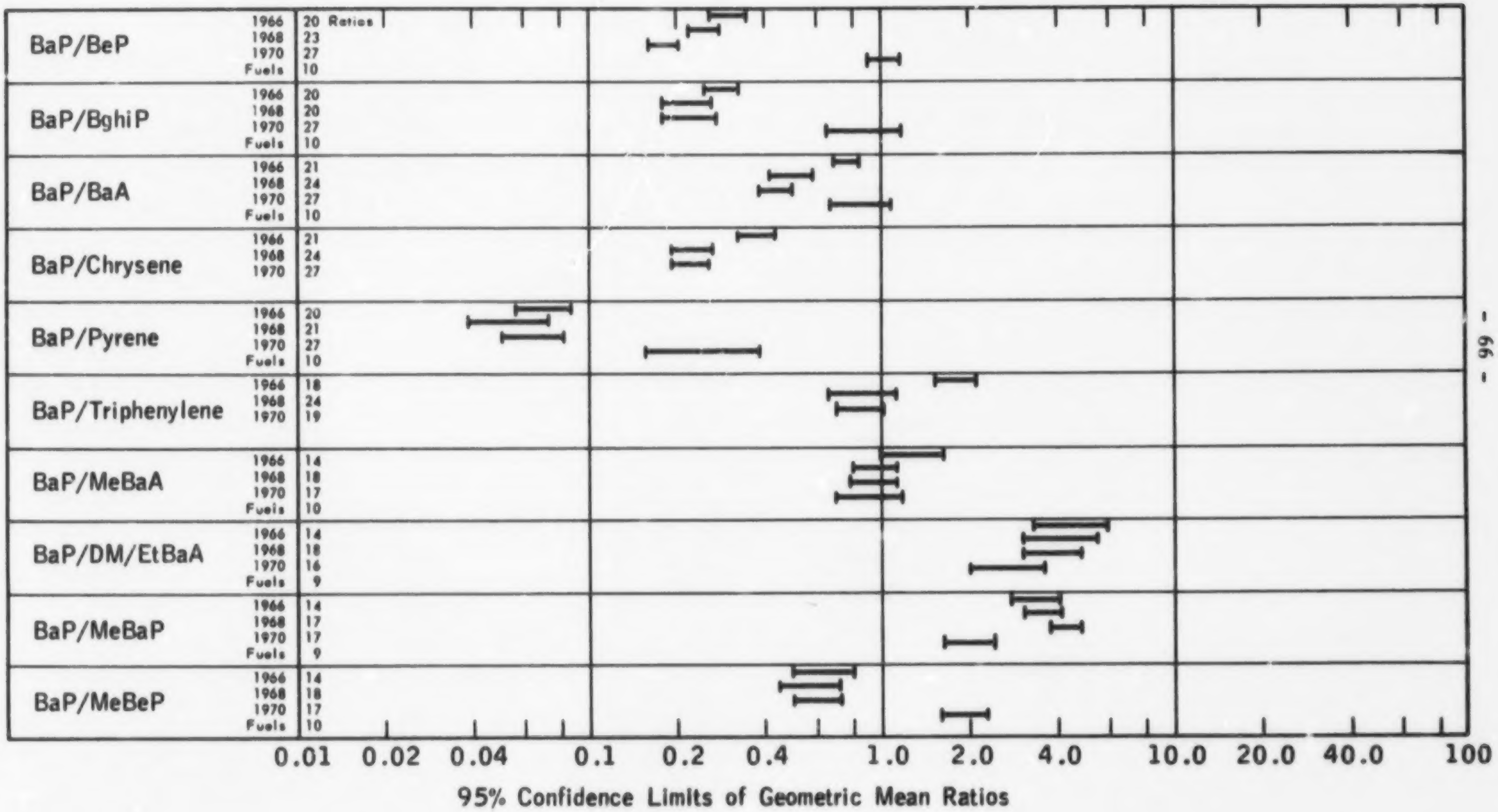
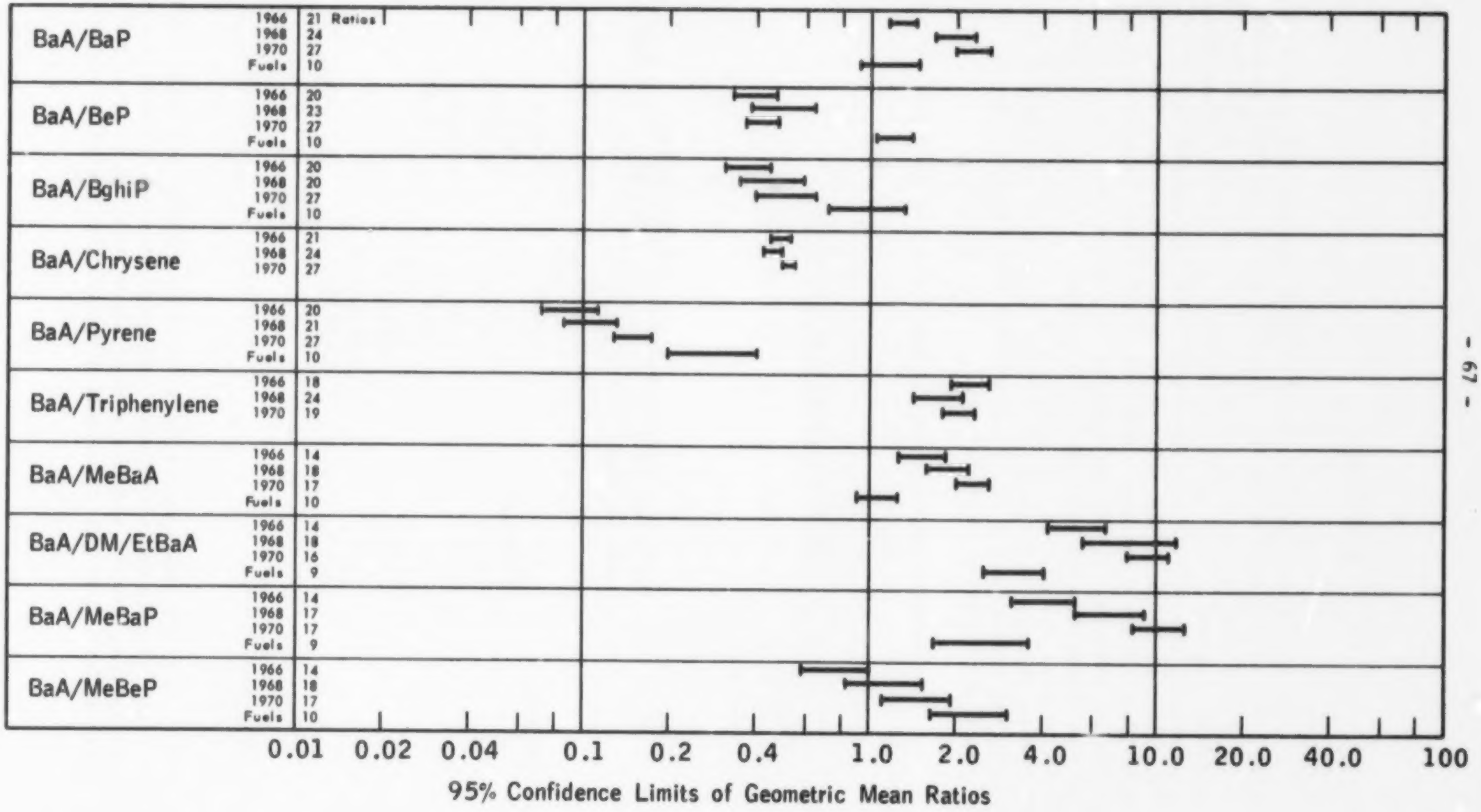


Figure 5

RATIOS OF BENZ(a)ANTHRACENE TO OTHER PNA
IN EXHAUST SAMPLES AND GASOLINES



It is clear from Figures 3 through 5 that there is much less between-vehicle difference in the value of any given mean species ratio than exists between the value of a ratio for fuels and its value for the three vehicles as a group. The chemical "severities" of the three exhausts are roughly equal, but differ substantially from the conditions for the synthesis of PNA found in fuels. The figures do indicate however, that some ratios changed significantly between vehicles, while many others changed by less-than significant amounts. It is reasonable to assume that the maximum difference in exhaust severity, or maximum ratio changes, will occur between the 1966 and 1970 vehicles. Ranking of the magnitudes and directions of these "1966 vs. 1970" ratio changes in Figures 3 through 5 permits additional estimates of the relative reactivities of the different PNA species, as was done above for the "fuels vs. vehicles" comparisons.

These new estimates are listed, with the previous estimate, in the following table.

RELATIVE REACTIVITIES OF PNA

(Decreasing Reactivity)

	Basis for Estimates			
	Fuels vs. 1970 Vehicle, Fig. 3 (BeP)	1966 vs. 1970 Vehicles		
		Fig. 3 (BeP)	Fig. 4 (BaP)	Fig. 5 (BaA)
Most Reactive	MeBaP	MeBaP	MeBaP	MeBaP
	DM/EtBaA	BaP	(BaP)	MeBeP
	MeBaA	Pyrene	MeBeP	BaP
	BaP	MeBeP	Pyrene	DM/EtBaA
	BaA	BghiP	DM/EtBaA	Pyrene
	MeBeP	DM/EtBaA	BghiP	MeBaA
	Pyrene	MeBaA	MeBaA	BghiP
	BghiP	Chrysene	BeP	BeP
	(BeP)	(BeP)	Chrysene	Chrysene
	--	BaA	BaA	(BaA)
Least Reactive	--	Triphen.	Triphen.	Triphen.

The three rankings based on between-vehicle changes are very similar and would be identical if no species results had been missing in the original input data. Only the species beyond the horizontal lines reacted to a significantly greater (or less) extent than the reference compound (in parentheses) in moving from the "severity" of the 1966 exhaust to that of the 1970 exhaust. The overall trend is as expected: BaP and MeBaP are most reactive and triphenylene has the least reactivity. Compared with the theoretical predictions and with the fuel-vehicle ranking, there are also some unexpected changes, however. BaA now seems to be much less reactive than BaP and is similar to chrysene and triphenylene; the alkyl derivatives of BaA also show decreased reactivities. Conversely, pyrene, BghiP, and MeBeP show increased reactivities.

The meaning of these changed rankings is not clear. One implication might be that an emission-controlled vehicle (1970, e.g.,) would control BaA emission somewhat less well than BaP emission relative to an uncontrolled vehicle. The data in Table 11 suggest a slight trend in this direction, but the difference is not large. Relative to the 1966 vehicle, the 1970 vehicle reduced BaP by 79-84% and reduced BaA by 54-76%, but with most of the BaA reductions at 72-76%. Along the same line, comparisons of species ratios for the experimental thermal-reactor vehicle (RAM) with the mean ratios for the 1968 Chevrolet show that the RAM apparently controlled the emissions of BeP and BaA a little less effectively than those of BaP, etc. In the overall view, however, the emission control systems (both current EM and experimental) reduced all PNA species so much, relative to the uncontrolled vehicle, that any fine-scale variations in reduction are not really significant.

This study of PNA ratios has a broader implication than relative reactivities , in any case. The values of each ratio for exhaust samples, from all three vehicles and many tests, were relatively constant, while differing significantly from their values in fuels. This suggests that different sources (coke ovens, coal furnaces, etc.) may give different characteristic PNA ratios. This suggests, in turn, that it might be possible to define the source of airborne PNA in a given location by comparison of its ratios with those from likely sources in the area. This possibility has already been suggested by Commins(16). Valid results would, of course, require maximum precautions against losses of certain species during sample collection. This has already been noted as an apparent problem in the CAPE-6-68 work, for example.

6.3 Ratios Between PNA Species vs. Sampling Losses

Throughout Project CAPE-6-68, the effects of controlled variables have been measured by differences in measured emissions of BaP and BaA. We now see that BaP and BaA are among the most reactive of all the PNA species for which analyses are available. (Only BaP and BaA analyses were available on early tests.) Also, in Section 7, experiments are reported that indicate that losses of BaP and BaA, in particular, were very likely to have occurred during collection of CAPE-6 samples, apparently because of their reactivities. On the other hand, tracer BaP and BaA were used in sample analysis, so that any losses of BaP and BaA after tracer addition would be taken into account more accurately than the losses of other species.

It is thus appropriate to inquire whether, because of reactivity and losses, BaP and BaP analyses are more variable than the analyses of less-reactive species. For this purpose, a variety of PNA species ratios were selected which included species with reactivities (in the ranking given by Tipson(7)) ranging from "both high" to "both very low". For each vehicle, computer analysis gave the number of values and the standard deviation in the determination of a single value of the $\log_{10}$ of each selected ratio. These standard deviations were then pooled over the three vehicles to provide an overall measure of variability in the determination of each ratio. The following table summarizes the results obtained.

VARIABILITY IN PNA RATIOS

Ratio	Standard Dev. in Log_{10} of Ratio	Reactivities	No. of Ratios in Pool
BaP/BaA	0.1548	Both High	72
BaP/Chrysene	0.1647	High/Very Low	72
BeP/MeBaP	0.1476	Low/Very High	48
BaA/BeP	0.1773	High/Low	70
Chrysene/BeP	0.1801	Very Low/Low	70
BaP/MeBaP	0.1346	Both High	48
BeP/MeBeP	0.1602	Both Low	49
Chrys./Triphenylene	0.1490	Both Very Low	61

There is no evident tendency for higher variability in ratios with mixed reactivities. This implies that losses, or other sources of inaccuracy in the exhaust emission results, are no more of a problem for BaP and BaA than for the other, less-reactive species, in the analyses. It follows that the Project's conclusions as to the effects of controlled variables are no less valid because they were based on the measured emissions of two of the most reactive species.

6.4 Repeatability of Analyses (Quality Control)

The repeatability of analyses of PNA in a given sample has been routinely monitored at Esso Research. The results obtained are clearly relevant to the questions of variability and accuracy discussed above, but also depend on the stability of stored samples. Table 24 summarizes results obtained over an 18-month period on samples of the supernatant liquid above solids removed from a heat-exchanger that had been in extended use to

Table 24

QUALITY-CONTROL SAMPLE FOR GC/UV PNA ANALYSIS

(Solids, in cyclohexane, removed from a heat exchanger processing raw exhaust to composite-sample bags.)

Units: µg of PNA in 50 ml of solution.

Sample No. Date Anal.	1 4/5/71	2 5/19/71	3 6/10/71	4 10/22/71	5 2/1/72	6 5/16/72	7 10/12/72
Pyrene	690.8	694.9	688.1	630.2	634.9	670.9	679.7
BaA	120.8	114.8	121.9	107.1	112.9	112.0	114.3
Chrysene	116.8	122.8	95.7	124.1	133.7	117.0	77.1
Triphenylene	26.6	23.4	25.8	25.4	26.3	25.2	27.2
Methyl BaA	59.4	62.1	60.6	51.6	53.3	54.7	60.0
DiMe/Et BaA	22.0	12.5	14.7	12.6	11.6	10.7	13.6
BaP	15.8	14.6	14.7	12.1	10.5	11.1	9.6
BeP	154	155.8	159.8	137.4	160.9	164.8	150.4
Benzo(g,h,i)Perylene	155.8	155.9	130.6	158.6	157.1	85.7	91.8
Methyl BaP	2.8	2.9	3.8	2.7	0.9	2.0	2.9
Methyl BeP	66.6	66.1	65.0	55.3	58.9	59.1	63.3

process raw exhaust to composite-sample bags at an emissions dynamometer installation. The liquid samples were all removed at the same time and stored in the dark, with air present, in nearly-full sealed amber bottles. Each analysis uses new additions of tracer BaP and tracer BaA. The data show generally excellent repeatability for many of the species determined. However, BaP and BghiP (but not MeBaP) show evidence of losses with time. At present, we can only suggest that these are true losses due to oxidation. The amounts of BaP and MeBaP in the sample have always been low, relative to both BeP and BaA. This is in line with their reactivities and the long exposure of the original solids to a wide variety of exhausts transitting the exchanger. The further losses of BaP (but not MeBaP) and, recently, of BghiP on storage in solution have no obvious explanation.

7. SELECTIVE LOSSES OF PNA SPECIES IN EXHAUST SAMPLES

7.1 Summary of Loss Studies

Within the framework of the CAPE-6-68 Program, several emission-test samples have been analyzed for PNA content in separate parts derived from (1) extracts of filter media at the collector outlet, (2) extracts of aqueous condensate at the heat-exchanger outlet, and (3) the washings from metal surfaces extending from the vehicle muffler to the filter frame, i.e., the balance of a normal sample, which is made up of a composite of the three parts. The relative amounts of different PNA species found in these different areas, together with exposures of pure PNA specimens (BaP, BaA, and benzo (e)Pyrene (BeP)) to the environment of the cool, filtered, outlet gases, prove that very substantial losses of certain reactive PNA species deposited on the outlet filter do occur in normal CAPE-6 sample-production procedures. Specifically, the apparent total yields of BaP and BaA and their alkyl derivatives are estimated to be only about 50% of the amounts actually emitted from the vehicle. The more stable BeP does not undergo this type of loss. In further work, growing out of this discovery and supported substantially by Esso Research and Engineering, an apparently effective technique for avoiding these losses has been demonstrated. This Section reports the experimental work related to these losses and the avoidance of the losses.

7.2 Evidence for CAPE-6-68 Losses

In Section 6 of this report, we have already mentioned the review by Tipson(7) of published theoretical and experimental studies on the relative reactivities of a variety of PNA species, including six determined in the CAPE-6 exhaust samples:

RELATIVE REACTIVITIES OF CAPE-6 PNA

(From Tipson, for Ortho Reactions)

PNA Species	Relative Reactivity
Benzo(a)pyrene	12
Benz(a)anthracene	5
Pyrene	3
Benzo(e)pyrene	<1
Chrysene	0.09
Triphenylene	10^{-6}

A similar ranking can be developed for single-point attack on the molecules. Apparently, BaP and BaA, which are the primary species determined in CAPE-6, are especially likely to react and, hence, to be lost from the samples. The alkyl derivatives of BaP and BaA can be expected to react similarly to their parent compounds.

Accidents affecting parts of the samples from CAPE-6 Tests 68, 78, and 79 made it necessary to separately analyze portions of the samples for Tests 69 (water extract) and 80 (filter extract), and three-part analyses of the samples for Tests 83 and 85 were also made to substantiate the indications of the Test 69 and 80 analyses. For each test, a total yield for each species is available (Table 22, Section 6) as the sum of the parts. In the following table, the amount of each species in each location in the apparatus is stated as a % of the total.

PNA SPECIES LOCATION FOR DIFFERING REACTIVITIES

	% Of Total In Each Location(a)					
	Water Extract			Filter Extract		
PNA Species	T69	T85	T83	T80	T85	T83
BaP	13.9	12.5	38.5	14.0 (b)	2.0 (b)	17.0 (b)
MeBaP	10.7	13.9	23.2	6.7 (b)	3.1 (b)	9.0 (b)
BaA	14.1	13.5	24.3	18.0	8.0	32.8
MeBaA	13.3	14.9	27.1	13.4	6.0	34.7
DM/EBaA	8.9	19.5	26.1	37.7	5.2(b)	23.1
BghiP	7.1	6.6	15.7	34.7	34.4	27.4
Pyrene	7.5	6.5	20.1	43.0	62.1	44.5
BeP	6.7	6.2	11.7	47.4	53.7	67.7
MeBeP	7.2	7.4	9.6	32.9	50.2	37.6
Chrysene	6.4	4.5	16.1	45.6	66.3	53.3
Triphenylene	5.5	4.3	15.4	57.4	66.9	54.6

(a) Tests 69, 80, and 85 in 1966 Plymouth; 83 in 1970 Chevrolet. The balance of each sample is in the washings of metal surfaces, etc.

(b) Low UV absorbance of solution of trapped GC peaks reduces accuracy.

These results suggest superficially that BaP and BaA and their derivatives are more effectively collected in the aqueous condensate than are BeP, chrysene, and triphenylene. This conclusion is difficult to accept, however, because these isomers (BaP and BeP; BaA, chrysene, and triphenylene) are not even separated, in general, by gas chromatography. The correct meaning of the results, in view of the reactivity differences, is rather that the reactive BaP, BaA, and their derivatives that are collected on the filter media are largely destroyed by reactions, either during or after collection of the sample. This depresses the totals and inflates the apparent % found in the aqueous condensate (and suspended soot particles).

If it is assumed that the condensate for a given test should contain about the same fraction of all species, and that no losses occur in the condensate, then it follows that the true total yields of BaP, BaA, and their derivatives were about twice as great as the apparent total yields. Furthermore, since more than one-half of the total of each stable PNA species is found on the filter, but little of the reactive species, it follows that losses of as much as 90% of the reactive PNA that are on the filter may be occurring. It is significant that BeP/BaP ratios, etc., in the filter are invariably high.

7.3 Confirmatory Tests of Losses

In order to describe experiments to confirm this hypothesis, and to develop a technique for loss-prevention, it is necessary to review briefly our standard CAPE-6 procedure. The vehicle was connected, without known leaks or openings, to the PNA collector inlet (diverter valve) before start-up. After starting, the diverter was turned from waste to the collector and was returned to waste (collector sealed) at the end of each of the three cold-start 12-cycle blocks used for sample production. The collector outlet was connected continuously to a positive-displacement pump with automatic air-bleed, which ensured against any back-pressure on the vehicle from the pressure-drop of the collector system under varying gas flows. After the third block, which occurred late in a working day, the pump was detached and the collector was sealed by a blanking plate, leaving the sample exposed to gases from the final deceleration. The system was opened, and the filter media removed to a glass jar, no sooner than the next day. In some cases longer residence occurred before filter removal, but no records are available on this point. The aqueous condensate was collected in a sidearm receiver, where it was isolated from the main gas flow, and was removed, after each block, to a larger vessel, along with any entrained soot. An after-test acetone rinse of the receiver vessel was combined with subsequent washings from metal surfaces because acetone interferes with analysis if present in the condensate. A diagram and photographs of the equipment appear in the First Annual Report.

The standard experiment used for loss-investigation and loss-prevention experiments has consisted of hanging two (replicate) Dexiglas (absolute filter media) strips, 12" x 1.5", on the outlet side of the sample collector filter. Each strip contained separate spots, about 1" in diameter, of pure PNA (BaP, BaA, BeP); typically, 10 μg of each was applied in cyclohexane solution. BeP was included in only a few experiments. Reference strips, held in the dark, or exposed to the same light but not to exhaust gas, and/or reference solutions at standard dilutions of the same amount of PNA, were also prepared, with some variations in practice in different experiments. In some experiments, a small amount of n-hexadecane, as an inert medium for the PNA, was incorporated in the spots, but this had no apparent effect.

After a test, the strips were removed (usually the next day, but within an hour in some later tests), cut in squares, and each square extracted, filtered, and diluted to 30 ml. with cyclohexane for UV absorbance measurement. Blank squares were also extracted (no spectra, but a background envelope) and the extracts used in the reference cell of the UV instrument. PNA recovery was judged by the absorbances of defined peaks (383, 332, and 289 nm for BaP, BeP, and BaA) above standard baselines. Even with severe losses, no new spectra were observed, nor did the spectral curves change beyond lowering and slight broadening of peaks.

The data obtained in these tests are summarized in Table 25. The table includes results from exposing a concentrate (for GC/UV analysis) left from CAPE-6 Test 73. This concentrate, in solution, had definite UV peaks and measurable tracer activity. This was also true of the extracted spots after exposure. As noted in footnote (d) of the table, the activity and prior analysis permitted some additional interpretations of the results to be made.

Recoveries of PNA by extraction of reference (unexposed) spots did not exceed 90% for BaP and BaA, but were very good for BeP and for the Test 73 composite sample. Some low recoveries (to 25% for BaA) in light-exposed reference strips remain unexplained, since carefully-controlled light-exposure experiments involving more-than-usual light exposure showed no effects for different kinds of light.

The most significant conclusions to be derived from Table 25 are that losses of up to 95% of the BaP and 80% of the BaA, but little or no loss of BeP, do occur in the filter-box environment. These conclusions are in line with the reactivity predictions and with the interpretation of the GC/UV sample analyses and locational variations presented earlier in this Appendix. The losses evident in the exposure data on the Test 73 concentrate are somewhat at variance with the analyses of extracts of the main filters, however. It appears that BaP, MeBaP, and benzo(ghi)perylene (BghiP) were all lost in the exposure, yet substantial BghiP was found in the filters of Tests 80, 83, and 85. (Tipson does not present estimates of the reactivity of BghiP.) Also, the exposed Test 73 concentrate did not seem to lose BaA and its derivatives, whereas they were apparently reduced in the filter extracts of the tests, and were lost to some extent, but less than BaP, in the exposed strips of Dexiglas.

7.4 Loss-Reduction Experiments

Table 25 includes results on PNA loss from exposures in Test 89B that are particularly meaningful as guides to a successful solution to the loss of PNA from filter samples. Independently of the other test objectives, including the exposures, a large-volume (to 170 CFM) flow of air through the entire collector system was created for several minutes at the end of the test. This was done to obtain pressure-drop data at various fixed flow rates. The PNA-exposure specimens were removed from the filter on the following day. In contrast to later tests without the air-flushing, these specimens showed no loss of BaA and significantly reduced losses of BaP. This suggested that purging shut-down gases from the system was desirable. (In this case, shut-down gases had been in contact with the specimens during vehicle cool-down after test-blocks 1 and 2.)

With this suggestion, Esso Research has used the PNA collector system in slightly different tests which have demonstrated a substantial reduction in the loss problem. A different test vehicle, with uniform deposits and with

Table 25

CAPE-6-68
RECOVERIES OF PNA SPECIES AFTER VARIOUS EXPOSURES

(Solution of each specimen deposited on Dexiglas filter, exposed, and extracted for UV assay, with the extract of an exposed blank filter in the reference cell.)

		Recoveries from Duplicate Filter Media Strips, %			PNA Concentrate (for GC/UV) from Test No. 73, exposed in Test 94, using UV absorbances at definite peaks above defined baselines. Recovery in %.			
Exposure	CAPE-6 PNA Test No.	Benzo(e)pyrene	Benzo(a)pyrene	Benz(a)anthracene	383 nm (d)	335 nm	318 nm	288 nm (d)
Filtered Gas in Collector Outlet	89B(a)	101,93	44,53	94,94	-	-	-	-
	90	106,92	19,25	67,43	-	-	-	-
	93	90,94	5,5	58,54	-	-	-	-
	94	-	11,11	22,19	0,0	83,85	71,74	96,92
Samples held in the dark after preparation (b). (No. of samples)		90,103 (2)	79 to 90 (4)	74 to 90 (4)	103	102	96	101
Samples exposed 2-5 min. to various lights (b,c). (No. of samples)		83,97 (2)	53 to 91 (12)	25 to 77 (12)	104,101 (2)	104,97 (2)	98,90 (2)	107,100 (2)

(a) Test 89B main sample was sooty because of over-choking in 2 of 3 starts. The PNA exposure tests in 89B were unique in that the entire collector unit was flushed with a large volume of air for several minutes after the test. Normally, no flush occurs, and the filters remain in place at least overnight.

(b) All specimens were prepared and extracted under gold (F40 GO) fluorescent lights, having no UV component.

(c) Light exposures included sunlight, F40 GO and F40 CW fluorescents, and G.E. H400 C33-1 mercury-arc light and, also, each of these filtered through amber, UV-opaque, plastic film. No differences, or effects, for lights were consistently observed.

(d) Radiotracer counts and prior GC/UV analyses show that about half of the 288 nm absorbance is due to BaA, MeBaA, and DMe/EtBaA, while all of the 383 nm absorbance is due to BaP+MeBaP+BghiP; all evidence of the latter (383 peak) was destroyed by exposure to filtered gas.

the same fuel used for both deposits and emission tests, was operated in three single 23-minute cold-start tests with the 1972 emission-test driving cycle. Duplicate speciments of BaP and BaA were present in the filterbox for each test. The start-up for each test had the diverter valve already open to the collector, but different procedures for sample collection were used thereafter:

(1) Like CAPE-6, the collector was sealed at shutdown and opened the following day.

(2) At shutdown, room air was drawn through the system (tailpipe disconnected) for 4 minutes at 175 CFM (measured after water-vapor removal in the cold exchanger), and the specimens were removed within one hour.

(3) A fixed outlet gas flow of 120 CFM was maintained throughout the test, combining (at a large T) air filtered through charcoal and paper (CVS filter element) with whatever exhaust was produced by the vehicle; i.e., a "CVS system" at 120 CFM total flow, followed by cooling and filtering, was created. After the test and 1 minute of air flow, the exposure specimens were removed within one hour.

The data obtained in these experiments are presented below. It appears from the data that both of the changes in procedure were effective in avoiding the loss of BaA from exposed specimens, while the CVS-type procedure (constant dilution) was slightly superior with respect to avoiding BaP loss.

ESSO RESEARCH TESTS ON PNA LOSSES
(Single 23-Minute 1972 FTP Tests)

	% Recovered					
	BaP			BaA		
Specimen	(1) Like CAPE-6	(2) Flush and Remove	(3) Dilution and Remove	(1) Like CAPE-6	(2) Flush and Remove	(3) Dilution and Remove
Ref. Solution	100	100	100	100	100	100
Held in Dark	91	-	89	91	-	90
Specimen #1	32	72	89	67	88	88
#2	35	68	91	62	86	87

It was felt, in planning these experiments, that the air-diluent cooling (item (3) above) and further cooling in the heat exchanger would minimize any losses of PNA from oxidation reactions. It was recognized, however, that air dilution to a total flow of only 120 CFM (to avoid excessive pressure drop in the system) would not give substantial diluent cooling in acceleration driving modes.

In general, this assumption appears likely to have been justified, but the relevant data require some qualification to arrive at this view. Esso Research has made available in Table 26 the emissions results, in µg/gal of fuel, for each of these three vehicle tests. The results for the air-dilution experiments (Column 3) are unexpectedly low for all PNA species, whether reactive or not. As noted in footnote (b), this is tentatively ascribed to an unexplained failure to reproduce vehicle conditions. (An across-the-board loss of all species by reactions with the diluent air is not consistent with known differences in PNA reactivities.) Arbitrarily doubling all of the PNA-emission values in the third column gives the "corrected" values in the fourth column of Table 26. Comparison of these values with those in the second column of figures indicates that only BghiP, MeBaA, and MeBaP appear to have been depressed by reactions with diluent air. Of these, both the MeBaA and MeBaP results are of relatively poor accuracy (footnote (c)). Their GC peaks, as well as their UV spectra, did show that their emission rates were indeed low, however, so the apparent losses cannot be fully discounted.

With the above qualification and the presumption that the three tests can be validly compared, then the most significant result from Table E-2 is the evidence of losses in the procedure that most nearly equalled CAPE-6 operation. All species except triphenylene, chrysene, and BeP underwent apparent losses relative to the air-flush test of 34% (pyrene) to 74% (DM/EBaA), with the losses in BaP and BaA amounting to 66% and 53%, respectively. Losses of this magnitude are consistent with the previously-described analyses of emission samples from different parts of the collector unit, and with the losses of pure PNA exposed in the filter-box outlet gas.

7.5 Future Practice in CAPE-6-68 Sampling

These experiments suggest that air-flushing after each vehicle operation period, and early filter removal, would be a relatively simple but improved procedure for future use in CAPE-6 or any similar project. However, such a change would increase the expected results of any test and would destroy its comparability to earlier data. For this reason, the limited further research planned by CAPE-6 will continue to use the existing procedure, without air-flushing, and to base conclusions primarily on changes in BaP and BaA emissions.

This decision is fully consistent with the objective of CAPE-6-68 to evaluate the relative effects on vehicle PNA emission for various changes in controlled fuel and vehicle variables. Section 6 has already shown that the ratios between reactive species (BaP, BaA, etc.) and non-reactive species (BeP, etc.) are no more variable than the ratios between two non-reactive species. This implies either reproducible losses of reactive species, or compensating sources of variability in determining non-reactive species. In either case, the use of either type of PNA should give equally valid measures of the effects of variables.

TABLE 26

ESSO RESEARCH TESTS ON PNA COLLECTION TECHNIQUES

(One vehicle, tested three times, with constant fuel and with engine deposits reproduced, in single 23-minute 1972 FTP tests.)

	Emissions in µg./gal. of Fuel Used			
PNA Species, in Order of Decreasing Reactivity (a)	Like CAPE-6; Sealed Overnight	Air-flush at End; Early Filter Removal	Air Dilution; Early Filter Removal	
			Observed	Corrected (b)
MeBaP	3.4(c)	8.6(c)	1.7(c)	3.4(c)
DM/EtBaA	2.6	10	6.4	12.8
MeBaA	15	42	1.9(c)	3.8(c)
BaP	20	59	30	60
BghiP	162	457	112	224
BaA	47	100	56	112
MeBeP	40	65	34	68
Pyrene	1050	1602	1010	2020
BeP	228	239	116	232
Chrysene	126	124	70	140
Triphenylene	40	35	22	44

(a) Ranking is based on observations of relative changes of species in a large number of CAPE-6 fuel and exhaust samples, with exhausts varying in temperature and oxygen content. The ranking of six major species agrees with Tipson's review, and alkyl derivatives are, as expected, more reactive than parent compounds.

(b) As a measure of avoiding PNA losses, the reduced PNA level (all species) in the third column is almost surely incorrect for non-reactive species at least. The corrected values compensate an apparent deficiency of 50% on all species, tentatively ascribed to failure to reproduce vehicle conditions. With this correction, the results for the non-reactive species conform to the other tests.

(c) Result is of low accuracy because of very low absorbance in the UV spectrum of the trapped GC peak.

7.6 Tracer Injection for Improved Accuracy

The foregoing work on sampling losses was largely carried out in the period following the presentation of SAE Paper 720210 (Reference 1a) in January, 1972, and the earlier work had not been fully evaluated by that time. In prepared comments on that presentation, Griffing(11) questioned the accuracy of the CAPE-6 emission results and suggested that losses were occurring after sample collection. Griffing had injected tracer BaP, vaporized in hot nitrogen, into vehicle exhaust enroute to a large partially air-filled plastic bag. After a necessarily brief vehicle run, a portion of the bag's contents, pumped through a filter, yielded a sample for BaP analysis and counting. These results, with the known tracer BaP addition, gave estimates of the BaP emitted by the vehicle. Apparently no other PNA species were determined.

The Griffing procedure requires, of course, that the fates of the thoroughly-mixed engine-emitted BaP and tracer BaP be the same after injection, including residence in the sample bag. Hoffman(9) had reported results, using a collector like the CAPE-6 collector, which raised some question as to the validity of this assumption in the case of exhaust from the tailpipe of a test vehicle on a dynamometer. Specifically, Hoffman indicated variable specific activities (DPM/μg) for BaP from different parts of his collector system. By analogy, whatever "part" was sampled from the collector bag in the Griffing procedure could control the result obtained. Griffing(13) had not ignored this question, however: Different amounts of injected tracer and different volumes of gas filtered from the bag were said to give equivalent BaP emission results in replicate vehicle tests. Also, Griffing noted that BaP losses did actually occur during residence in the collector bag.

Griffing suggested(13) that total-collection systems, such as were used by Begeman(5), Hoffman(9), and CAPE-6-68, should be validated by the addition of a tracer-BaP-in-nitrogen system for tailpipe injection. Assuming the solution of the very substantial technical problems implied, including radiation hazards, and assuming that the implications of Hoffman's experience (see above) can be avoided by using a total sample, the suggestion has some merit. However, the CAPE-6 loss-experiment results, showing losses which vary for different PNA species, make it clear that the injection technique cannot be extended rigorously beyond the actual species that are injected. Furthermore, some assurance is required that, if more than one radioactive species is injected, there will be no thermally-induced interconversion or degradation of one active species to another.

In any case, and without taking into account the losses in the CAPE-6 procedure, the Griffing data and the CAPE-6 data do provide very similar estimates of the relative effects of different controlled variables on BaP emission. The discrepancies exist, as might be expected, in the estimates of absolute (μg/gallon or μg/mile) effects. Griffing does question(11) the ability of very-low-emission control systems to control PNA to the extent that CAPE-6 has described in this report. However, we have already indicated in Section 5 of this report the belief that the control systems used by Griffing for data that imply this question were not, in fact, as effective as those used by CAPE-6 so far as the control of CO and HC are concerned. Thus, they should not properly be compared as to PNA control.

The Griffing suggestion that PNA are being lost in the CAPE-6 procedure was, on balance, a valuable contribution in spite of the foregoing discussion. It served as a stimulus to carry out a variety of significant experiments on PNA losses and these, in turn, provided a much-improved insight into the limitations of CAPE-6 results in an absolute sense.

APPENDIX A

REFERENCES

(1) Gross, G. P., "Second Annual Report on Gasoline Composition and Vehicle Exhaust Gas Polynuclear Aromatic Content," (CRC-APRAC Project CAPE-6-68), Period Ending April 15, 1971. (NTIS Accession No. PB-209-955.)

(1a) Gross, G. P., "The Effect of Fuel and Vehicle Variables on Polynuclear Aromatic Hydrocarbon and Phenol Emissions," Paper No. 720210 at the SAE Automotive Engineering Congress and Exposition, Detroit, Mich., January 10-14, 1972. (Accepted for publication in 1972 SAE Transactions.)

(2) Gross, G. P., "First Annual Report on Gasoline Composition and Vehicle Exhaust Gas Polynuclear Aromatic Content," (CRC-APRAC Project CAPE-6-68), Period Ending February 17, 1970. (NTIS Accession No. PB-200-266.)

(3) Lang., R. J., "A Well-Mixed Thermal Reactor System for Automotive Emission Control," SAE Transactions, 80, 2148-2155 (1971).

(4) Lunt, R. S., III, Bernstein, L. S., Hansel, J. G., and Holt, E. L., "Application of a Monel-Platinum Dual Catalyst System to Automotive Emission Control," Paper No. 720209 at the SAE Automotive Engineering Congress and Exposition, Detroit, Mich., January 10-14, 1972. (Accepted for publication in 1972 SAE Transactions.)

(5) Begeman, C. R., and Colucci, J. M., "Polynuclear Aromatic Hydrocarbon Emissions from Automotive Engines," SAE Transactions, 79, 1682-1698 (1970).

(6) Brown, R. A., et al., "Final Report on Rapid Methods of Analysis for Trace Quantities of Polynuclear Aromatic Hydrocarbons in Automobile Exhaust, Gasoline, and Crankcase Oil, and Phenols in Automobile Exhaust," (CRC-APRAC Project CAPE-12-68), Period of February, 1969, to December, 1971. Report in preparation.

(7) Tipson, R. S., "Oxidation of Polycyclic, Aromatic Hydrocarbons - A Review of the Literature," U. S. National Bureau of Standards Monograph 87, issued September 17, 1965.

(8) *Federal Register*, 35 (219) Part II, p. 17288 et seq., November 10, 1970.

(9) Hoffman, C. S., Jr., Willis, R. L., Patterson, G. H., and Jacobs, E. S., "Polynuclear Aromatic Hydrocarbon Emissions from Vehicles," presented to Division of Petroleum Chemistry, Inc., American Chemical Society, Los Angeles, March 28-April 2, 1971. (Preprints, Vol. 16, No. 2, page E-36).

(10) Padrta, F. G., Samson, P. C., Donohue, J. J., and Skala, H., "Polynuclear Aromatics in Automobile Exhaust," presented to Division of Petroleum Chemistry, Inc., American Chemical Society, Los Angeles, March 28-April 2, 1971 (Preprints, Vol. 16, No. 2, page E-13).

(11) Griffing, M. E., Prepared Discussion of Reference 1a (SAE Paper 720210), presented at the SAE Automotive Engineering Congress and Exposition, Detroit, Mich., January 10-14, 1972. (To be published in 1972 SAE Transactions.)

(12) Begeman, C. R., and Colucci, J. M., "Benzo(a)pyrene in Gasoline Partially Persists in Automobile Exhaust," (letter), Science, 161, 271 (1968).

(13) Griffing, M. E., Maler, A. R., Borland, J. E., and Decker, R. R., "Applying a New Method for Measuring Benzo(a)pyrene in Vehicle Exhaust to the Study of Fuel Factors," presented to Division of Petroleum Chemistry, Inc., American Chemical Society, Los Angeles, March 28-April 2, 1971 (Preprints, Vol. 16, No. 2., page E-24).

(14) Griffing, M. E., Maler, A. R., and Cobb, D. G., "A New Tracer Technique for Sampling and Analysis of Exhaust Gas for Benzo(a)-pyrene, Using Carbon 14," presented to Division of Petroleum Chemistry, Inc., American Chemical Society, New York City, Sept. 7-12, 1969 (Preprints, Vol. 14, No. 3, page B-162).

(15) Moran, J. B., Prepared Discussion of Reference 1a (SAE Paper 720210), presented at the SAE Automotive Engineering Congress and Exposition, Detroit, Mich., January 10-14, 1972. (To be published in 1972 SAE Transactions.)

(16) Commins, B. T., "Formation of Polycyclic Aromatic Hydrocarbons During Pyrolysis and Combustion of Hydrocarbons," Atmospheric Environment, 3, 565-572 (1969).

(17) Oro, J., Han, J., and Zkatkis, A., "Application of High Resolution Gas Chromatography - Mass Spectrophotometry to the Analysis of the Pyrolysis Products of Isoprene," Analytical Chemistry, 39, 27-32 (1967).

(18) Cleary, G. J., "Polycyclic Hydrocarbon Ratios: Their Use in Studying the Sequence of Combustion in a Hand-fired Intermittent Brick Kiln," Proceedings of International Clean Air Congress, October, 1966, pp. 111-114, National Society for Clean Air, London.

(19) Badger, G. M., Kimber, R. W. L., and Novotny, J., "The Formation of Aromatic Hydrocarbons at High Temperatures. XXI. The Pyrolysis of n-Butylbenzene over a Range of Temperatures from 300° to 900° (C) at 50° Intervals." Australian J. of Chem., 17, 778-786 (1964).

(20) Federal Register, 31 (61) Part II, p. 5170 et seq., March 30, 1966.

APPENDIX B

EXHAUST-GAS TEMPERATURE AND COMPOSITION DATA

Table B-1 summarizes the hot-cycle muffler-exit exhaust-gas temperatures measured in the latter part of each emission-test block. (For details of test equipment and procedures, see the previous Annual Reports (1, 2) and Sections 3.2.1 and 3.3 of this report.) Averages of these gas temperatures were used in Section 3.2.1 as measures of vehicle exhaust conditions.

Average (over one to three of the three test blocks) values of corrected gas analyses (see Section 3.2.1) are given in Tables B-2 through B-41 for the CO, HC, and NO emissions in each mode of selected cold and hot cycles in each PNA-emission test. The composite results for CO, HC, and NO for each test also appear in Table 8.

TABLE B-1

EXHAUST-GAS TEMPERATURES

(Third-year data. Measured in hot cycles at muffler exit.)

		Muffler Exit, °F., min./max.		
Vehicle	Test No.	Block 1	Block 2	Block 3
1966 Plymouth	61	452/565	456/569	443/562
(NC)	61B	---/570	450/575	450/575
	62	440/555	446/560	445/558
	68	470/580	465/580	467/583
	69	467/597	463/594	462/590
	73	458/571	458/575	458/573
	76	447/560	445/562	446/563
	77	451/575	455/575	455/575
	77B	442/555	446/560	446/560
	80	435/545	433/546	433/545
	81	457/569	461/569	456/567
	85	441/560	441/561	445/565
	89	446/563	451/578	448/570
	89B	460/581	462/585	463/595
	93	466/592	467/594	460/588
	96	456/578	456/580	463/582
1968 Chevrolet	64	476/584	482/587	481/585
(EM)	65(a)	480/590	480/590	---/---
	71	495/610	496/610	494/608
	72	478/596	480/603	479/595
	78	483/595	482/600	472/587
	79	473/585	470/580	472/585
	82	464/575	476/576	462/571
	86	472/574	470/574	475/577
	90(b)	---/---	---/---	462/567
	92	483/595	487/600	475/580
	94	485/590	487/592	482/592
1970 Chevrolet	66	577/711	583/717	588/711
(EM)	67	583/715	577/715	573/710
	70	578/715	580/720	576/715
	74	585/719	582/720	580/725
	75	576/707	574/699	575/704
	83	555/675	561/680	560/680
	84	546/680	546/675	545/675
	87	562/691	560/695	556/695
	88	562/690	573/697	569/690
	91	556/667	560/672	572/676
	95	585/695	585/695	593/703

(a) Test included only two blocks.

(b) Thermocouple instrument defective in part of test.

TABLE B-2

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 60

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	.52	1.23	.25	.37	.24	.44	.27	
	2	.04	.05	.04	.02	.11	.11	.05	
	3	.07	.04	.02	.01	.07	.06	.02	
	4	.03	.03	.01	.01	.04	.03	.02	
	Avg. 1-4	.17	.34	.08	.10	.11	.16	.09	.17
	6	.05	.04	.01	.01	.02	.03	.01	
	7	.01	.01	.01	.01	.04	.03	.01	
	Avg. 6-7	.03	.03	.01	.01	.03	.03	.01	.01
	Composite Test Result, % CO								.07
IRHC, ppm (C_6)	1	79	46	5	8	3	5	1	
	2	2	2	2	2	1	2	1	
	3	2	1	1	2	2	1	2	
	4	3	2	2	2	1	1	1	
	Avg. 1-4	21	12	2	3	2	2	1	5
	6	7	5	3	3	3	3	0	
	7	5	5	3	5	3	3	3	
	Avg. 6-7	6	5	3	4	3	3	2	2
	Composite Test Result, ppm HC								3
NO, ppm	1	417	287	75	37	45	268	82	
	2	55	364	144	52	64	844	193	
	3	45	329	154	64	55	760	183	
	4	34	254	128	50	54	665	175	
	Avg. 1-4	138	309	125	51	54	634	158	392
	6	34	362	102	36	96	684	136	
	7	34	322	62	24	42	680	174	
	Avg. 6-7	34	342	82	30	70	682	156	413
	Composite Test Result, ppm NO								406

Note: CO and HC instruments were near their lowest useful limits; HC data were corrected for the separately-determined response of the instrument to CO_2 in the sample gas. Concurrent FID data confirm low HC values.

TABLE B-3

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 61

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	8.38	5.30	2.59	5.23	3.66	1.78	6.44	
	2	4.24	2.52	1.47	4.66	3.96	1.39	5.17	
	3	3.57	1.57	.48	2.82	3.31	.53	3.59	
	4	2.93	1.41	.66	2.93	3.77	.66	3.74	
	Avg. 1-4	4.78	2.70	1.30	3.91	3.68	1.09	4.74	2.05
	6	3.11	1.45	.91	3.02	3.96	.70	3.49	
	7	3.08	1.37	.88	2.90	3.98	.69	3.38	
	Avg. 6-7	3.10	1.41	.90	2.96	3.97	.70	3.44	1.36
	Composite Test Result, % CO								1.59
IRHC, ppm (C_6)	1	723	504	365	868	503	373	1271	
	2	423	407	373	430	487	353	1136	
	3	361	357	311	483	465	314	1227	
	4	329	330	316	566	489	301	1311	
	Avg. 1-4	459	400	341	587	486	335	1237	404
	6	322	318	303	647	479	293	1483	
	7	324	315	292	745	471	294	1475	
	Avg. 6-7	323	317	298	697	475	294	1479	368
	Composite Test Result, ppm HC								380
NO, ppm	1	44.6	583	903	369	403	1655	184	
	2	83.3	1157	1328	430	363	2042	370	
	3	111	1531	1509	525	429	2511	603	
	4	123	1549	1542	512	321	2476	603	
	Avg. 1-4	90	1205	1321	459	379	2171	441	1499
	6	99	1477	1179	432	207	2431	645	
	7	93	1439	1134	449	207	2440	665	
	Avg. 6-7	97	1459	1157	441	207	2435	656	1660
	Composite Test Result, ppm NO								1603

TABLE B-4

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 61B

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	8.71	4.83	2.57	5.21	3.55	2.20	6.65	
	2	4.04	2.63	1.58	4.70	4.19	1.56	5.80	
	3	3.61	1.78	.40	3.06	3.21	.46	4.10	
	4	2.60	1.17	.59	2.53	3.62	.64	4.11	
	Avg. 1-4	4.74	2.61	1.29	3.88	3.65	1.22	5.17	2.08
	6	2.92	1.40	.86	2.64	3.89	.68	3.72	
	7	2.90	1.36	.92	2.79	3.68	.65	3.81	
	Avg. 6-7	2.92	1.38	.89	2.72	3.79	.67	3.77	1.32
	Composite Test Result, % CO								1.58
IRHC, ppm (C_6)	1	780	528	415	966	558	411	1713	
	2	499	457	439	537	554	392	1532	
	3	439	411	372	540	466	356	1702	
	4	390	364	344	821	526	331	1823	
	Avg. 1-4	527	440	393	716	526	373	1693	462
	6	386	355	346	1055	521	325	1937	
	7	383	348	370	926	453	325	1955	
	Avg. 6-7	385	352	359	991	487	326	1947	433
	Composite Test Result, ppm HC								442
NO, ppm	1	29	700	1060	366	369	1497	181	
	2	70	1057	1281	418	258	1976	305	
	3	82	1460	1733	602	336	2605	476	
	4	98	1666	1439	603	296	2545	461	
	Avg. 1-4	70	1221	1379	497	315	2156	356	1499
	6	73	1573	1221	480	141	2556	559	
	7	65	1593	1200	413	114	2563	541	
	Avg. 6-7	69	1583	1211	447	128	2561	551	1744
	Composite Test Result, ppm NO								1658

TABLE B-5

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 62

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	7.50	4.59	2.30	5.02	3.35	1.74	6.49	
	2	3.82	2.44	1.38	4.38	3.82	1.40	5.57	
	3	3.46	1.82	.48	3.17	3.36	.44	3.62	
	4	2.50	1.14	.65	2.51	3.38	.53	3.95	
	Avg. 1-4	4.32	2.50	1.20	3.77	3.48	1.03	4.91	1.93
	6	2.80	1.31	.69	2.57	3.67	.52	3.66	
	7	2.92	1.36	.75	2.72	3.77	.60	3.81	
	Avg. 6-7	2.86	1.33	.72	2.65	3.73	.56	3.74	1.23
	Composite Test Result, % CO								1.47
IRHC, ppm (C_6)	1	668	484	357	763	503	366	1383	
	2	435	419	355	447	495	360	1173	
	3	379	361	326	391	495	323	1457	
	4	359	344	313	766	505	325	1550	
	Avg. 1-4	461	402	338	592	499	344	1391	412
	6	341	323	286	716	469	299	1521	
	7	329	311	287	743	473	295	1639	
	Avg. 6-7	335	318	287	730	472	297	1581	373
	Composite Test Result, ppm HC								386
NO, ppm	1	107	807	996	395	418	1709	166	
	2	73	1112	1262	454	341	2013	295	
	3	85	1379	1607	525	355	2577	594	
	4	91	1553	1378	501	284	2537	557	
	Avg. 1-4	89	1204	1311	469	350	2209	403	1512
	6	86	1466	1300	560	241	2640	583	
	7	75	1467	1307	509	226	2580	615	
	Avg. 6-7	81	1467	1304	535	234	2610	599	1762
	Composite Test Result, ppm NO								1674

TABLE B-6

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 63

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	.27	.62	.28	.16	.03	.17	.11	
	2	.02	.05	.03	.02	.03	.14	.07	
	3	.02	.03	.02	.01	.02	.07	.04	
	4	.02	.03	.02	.02	.01	.02	.01	
	Avg. 1-4	.05	.18	.09	.06	.02	.10	.06	.09
	6	.01	.02	.02	.02	.01	.02	.01	
	7	.01	.02	.01	.01	.01	.02	.02	
	Avg. 6-7	.01	.02	.02	.01	.01	.02	.02	.00
	Composite Test Result, % CO								.03
IRHC, ppm (C_6)	1	33	33	25	27	17	22	33	
	2	19	18	18	18	14	19	19	
	3	13	15	16	17	14	18	21	
	4	14	14	16	16	13	17	20	
	Avg. 1-4	19	20	19	20	14	19	23	15
	6	13	12	14	18	11	15	22	
	7	12	11	16	18	12	15	20	
	Avg. 6-7	13	12	15	18	12	15	21	12
	Composite Test Result, ppm HC								12
NO, ppm	1	163	129	95	83	75	149	60	
	2	22	38	105	74	25	124	50	
	3	18	34	59	43	13	107	43	
	4	14	48	45	28	12	100	57	
	Avg. 1-4	55	62	76	57	31	121	53	85
	6	19	100	55	19	27	242	83	
	7	23	127	37	14	46	280	109	
	Avg. 6-7	21	114	47	17	37	262	97	156
	Composite Test Result, ppm NO								130

TABLE B-7

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 64

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.12	4.65	4.17	3.60	3.28	1.15	2.44	
	2	1.04	.40	.20	2.60	.44	.25	2.49	
	3	1.79	.54	.19	2.21	.51	.27	2.10	
	4	1.56	.48	.20	1.95	.41	.23	1.96	
	Avg. 1-4	2.38	1.52	1.19	2.59	1.16	.48	2.25	1.08
	6	1.41	.49	.20	1.81	.36	.22	2.06	
	7	1.39	.44	.21	1.97	.58	.23	2.10	
	Avg. 6-7	1.40	.47	.21	1.90	.47	.23	2.08	.48
	Composite Test Result, % CO								.69
IRHC, ppm (C_6)	1	351	318	285	279	265	243	234	
	2	270	215	185	263	174	188	791	
	3	389	239	181	249	169	191	707	
	4	290	209	178	247	163	177	739	
	Avg. 1-4	325	246	207	259	193	199	618	230
	6	287	210	169	229	153	177	739	
	7	289	212	187	249	161	178	782	
	Avg. 6-7	288	212	179	239	157	179	761	209
	Composite Test Result, ppm HC								216
NO, ppm	1	245	315	267	294	313	1385	416	
	2	355	957	653	250	233	1448	465	
	3	178	1024	719	260	223	1597	470	
	4	184	961	696	241	218	1449	509	
	Avg. 1-4	241	814	584	261	247	1470	465	986
	6	201	1016	627	233	221	1434	527	
	7	202	1012	632	217	198	1463	503	
	Avg. 6-7	203	1015	630	225	210	1449	515	1026
	Composite Test Result, ppm NO								1012

TABLE B-8

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 65

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.1	5.44	6.66	5.67	5.61	2.66	3.56	
	2	0.86	0.41	0.42	3.21	1.09	0.25	2.62	
	3	1.65	0.55	0.21	1.81	0.48	0.31	1.86	
	4	1.47	0.54	0.23	1.57	0.48	0.21	1.80	
	Avg. 1-4	2.27	1.74	1.88	3.07	1.92	0.86	2.46	1.46
	6	1.30	0.48	0.22	1.62	0.46	0.24	1.73	
	7	1.26	0.46	0.22	1.66	0.43	0.22	1.89	
	Avg. 6-7	1.28	0.47	0.22	1.64	0.45	0.23	1.81	.44
	Composite Test Result, % CO								.79
IRHC, ppm (C_6)	1	296	276	252	251	240	206	200	
	2	190	162	130	191	134	144	364	
	3	224	157	111	162	110	123	461	
	4	210	152	118	176	116	124	492	
	Avg. 1-4	230	187	153	196	150	149	379	168
	6	207	148	105	158	107	118	526	
	7	207	148	102	175	108	119	600	
	Avg. 6-7	208	148	104	167	108	119	563	140
	Composite Test Result, ppm HC								149
NO, ppm	1	283	246	108	128	138	928	399	
	2	480	1068	704	264	206	1613	432	
	3	187	1013	729	259	254	1727	488	
	4	199	1036	776	257	238	1741	498	
	Avg. 1-4	288	841	579	227	209	1503	455	1002
	6	224	997	645	255	246	1613	525	
	7	213	1057	545	239	211	1596	528	
	Avg. 6-7	219	1028	595	248	229	1605	527	1100
	Composite Test Result, ppm NO								1065

TABLE B-9

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 66

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	.37	2.50	.23	1.41	.81	1.41	2.13	
	2	.60	.84	.16	.40	.18	.70	.60	
	3	.24	.68	.16	.30	.35	.70	.52	
	4	.34	.72	.16	.38	.22	.72	.58	
	Avg. 1-4	.40	1.18	.18	.62	.39	.88	.96	.78
	6	.58	79	.22	.50	.21	.71	.76	
	7	.54	.88	.24	.48	.23	.77	.66	
	Avg. 6-7	.56	.84	.23	.49	.22	.74	.72	.62
	Composite Test Result, % CO								.68
IRHC, ppm (C_6)	1	200	198	249	257	129	184	666	
	2	147	121	188	239	73	126	843	
	3	127	108	171	233	72	120	735	
	4	116	96	169	183	55	109	669	
	Avg. 1-4	497	287	193	229	83	135	728	212
	6	119	96	221	201	60	116	726	
	7	114	105	181	213	60	131	728	
	Avg. 6-7	117	101	202	208	61	124	727	144
	Composite Test Result, ppm HC								167
NO, ppm	1	52	256	726	299	157	720	366	
	2	129	474	820	372	176	910	460	
	3	193	533	969	428	191	1045	552	
	4	181	530	1014	415	191	959	514	
	Avg. 1-4	139	448	883	378	179	909	474	676
	6	171	456	858	449	182	929	481	
	7	177	525	906	446	171	1061	530	
	Avg. 6-7	174	491	883	448	177	996	506	734
	Composite Test Result, ppm NO								714

TABLE B-10

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 67

Data are averages from first 7 cycles of 1 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	0.28	2.58	1.74	2.10	0.49	1.71	2.47	
	2	0.68	0.57	0.15	0.39	0.20	0.45	0.52	
	3	0.17	0.43	0.15	0.20	0.12	0.43	0.37	
	4	0.22	0.48	0.14	0.21	0.12	0.51	0.42	
	Avg. 1-4	0.34	1.02	0.55	0.73	0.23	0.77	0.95	0.74
	6	0.30	0.48	0.14	0.28	0.16	0.41	0.48	
	7	0.28	0.43	0.15	0.27	0.19	0.38	0.52	
	Avg. 6-7	0.30	0.46	0.15	0.28	0.18	0.40	0.50	0.33
	Composite Test Result, % CO								0.47
IRHC, ppm (C_6)	1	273	206	217	195	83	139	255	
	2	101	79	130	134	54	86	357	
	3	82	66	117	124	40	79	373	
	4	75	69	121	119	39	79	417	
	Avg. 1-4	133	105	147	143	55	96	351	112
	6	77	62	133	153	39	76	490	
	7	81	65	121	147	47	83	471	
	Avg. 6-7	79	64	128	150	43	80	481	94
	Composite Test Result, ppm HC								100
NO, ppm	1	117	445	917	359	216	785	401	
	2	157	653	1387	573	217	1179	617	
	3	223	686	1318	619	225	1237	685	
	4	241	711	1383	622	215	1235	647	
	Avg. 1-4	185	624	1251	544	219	1109	587	871
	6	221	651	1305	615	195	1315	657	
	7	229	622	1281	607	197	1252	681	
	Avg. 6-7	226	637	1293	611	196	1285	670	966
	Composite Test Result, ppm NO								932

TABLE B-11

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 68

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	7.24	4.31	2.59	5.34	3.64	1.66	6.65	
	2	3.91	2.31	1.38	4.57	3.66	1.33	5.51	
	3	3.17	1.65	0.29	2.74	3.15	0.44	4.15	
	4	2.51	1.21	0.46	2.63	3.46	0.51	4.11	
	Avg. 1-4	4.21	2.37	1.18	3.82	3.48	0.99	5.11	1.86
	6	2.83	1.32	0.68	2.78	3.72	0.64	3.90	
	7	2.84	1.42	0.69	2.91	3.85	0.69	3.63	
	Avg. 6-7	2.84	1.37	0.69	2.85	3.79	0.67	3.76	1.30
	Composite Test Result, % CO								1.49
IRHC, ppm (C_6)	1	644	473	373	927	501	382	1549	
	2	564	497	449	526	487	376	1277	
	3	400	386	338	514	441	327	1441	
	4	361	361	323	651	445	308	1570	
	Avg. 1-4	493	430	371	654	469	348	1459	432
	6	350	336	298	717	456	296	1717	
	7	345	342	298	728	445	296	1532	
	Avg. 6-7	348	339	298	723	451	296	1625	380
	Composite Test Result, ppm HC								397
NO, ppm	1	119	855	1032	413	400	1782	206	
	2	96	1265	1473	434	442	2151	301	
	3	126	1581	1933	616	385	2718	492	
	4	134	1721	1709	584	343	2743	505	
	Avg. 1-4	119	1356	1537	512	393	2348	376	1645
	6	113	1662	1339	506	257	2605	582	
	7	108	1567	1503	485	228	2515	523	
	Avg. 6-7	111	1615	1422	496	243	2561	553	1788
	Composite Test Result, ppm NO								1738

TABLE B-12

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 69

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	8.93	4.93	2.57	5.36	4.14	2.11	6.46	
	2	4.40	2.72	1.17	4.07	3.91	1.37	4.95	
	3	3.58	1.46	0.50	2.68	3.48	0.55	3.74	
	4	3.10	1.39	0.47	2.93	3.87	0.62	3.84	
	Avg. 1-4	5.00	2.62	1.18	3.76	3.85	1.17	4.75	2.06
	6	3.38	1.54	0.93	3.06	4.26	0.81	3.85	
	7	3.42	1.48	0.78	2.98	4.07	0.73	3.81	
	Avg. 6-7	3.41	1.52	0.86	3.02	4.17	0.77	3.84	1.46
	Composite Test Result, % CO								1.66
IRHC, ppm (C_6)	1	943	594	421	1017	540	409	1597	
	2	495	477	401	455	507	373	1415	
	3	381	372	334	667	484	328	1641	
	4	369	349	339	715	481	324	1625	
	Avg. 1-4	547	448	375	714	503	359	1570	452
	6	362	337	334	715	485	315	1743	
	7	357	330	307	823	460	301	1785	
	Avg. 6-7	360	334	321	769	473	309	1764	395
	Composite Test Result, ppm HC								415
NO, ppm	1	23	598	921	321	279	1464	209	
	2	65	1030	1273	416	304	1963	319	
	3	86	1436	1639	560	341	2499	429	
	4	92	1424	1503	521	204	2398	443	
	Avg. 1-4	67	1137	1335	455	282	2081	350	1435
	6	77	1453	1130	418	188	2239	444	
	7	73	1400	1156	452	195	2330	459	
	Avg. 6-7	75	1427	1143	435	192	2285	452	1574
	Composite Test Result, ppm NO								1525

TABLE B-13

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 70

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	0.62	3.65	2.06	2.36	1.12	2.60	2.84	
	2	1.29	1.17	0.23	0.88	0.54	0.81	0.81	
	3	0.61	0.83	0.18	0.46	0.23	0.84	0.65	
	4	0.50	0.82	0.17	0.43	0.28	0.83	0.64	
	Avg. 1-4	0.76	1.62	0.66	1.03	0.55	1.27	1.23	1.18
	6	0.69	0.87	0.19	0.54	0.35	0.81	0.71	
	7	0.73	0.85	0.21	0.57	0.35	0.76	0.75	
	Avg. 6-7	0.71	0.87	0.21	0.55	0.35	0.79	0.73	0.67
	Composite Test Result, % CO								0.85
IRHC, ppm (C_6)	1	503	293	311	309	153	208	637	
	2	181	157	239	257	111	148	800	
	3	150	126	211	243	89	132	721	
	4	149	126	210	237	87	129	759	
	Avg. 1-4	246	176	243	262	110	155	729	192
	6	132	115	179	195	75	136	708	
	7	135	115	210	197	79	135	757	
	Avg. 6-7	134	116	195	197	77	136	733	154
	Composite Test Result, ppm HC								167
NO, ppm	1	121	279	761	281	189	549	332	
	2	135	498	1203	456	201	975	475	
	3	169	560	1324	528	214	1039	530	
	4	191	619	1331	547	211	1057	531	
	Avg. 1-4	155	489	1155	453	204	905	467	723
	6	173	531	1266	522	199	1080	512	
	7	179	539	1283	488	187	1076	553	
	Avg. 6-7	177	535	1275	505	193	1079	533	833
	Composite Test Result, ppm NO								794

TABLE B-14

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 71

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.03	4.76	6.02	4.88	4.71	2.17	2.87	
	2	0.71	0.32	0.35	2.97	0.63	0.20	2.67	
	3	1.48	0.49	0.19	1.93	0.34	0.20	1.71	
	4	1.30	0.39	0.18	1.57	0.27	0.18	1.73	
	Avg. 1-4	2.13	1.49	1.69	2.84	1.49	0.69	2.25	1.25
	6	1.14	0.33	0.22	1.57	0.34	0.17	1.85	
	7	1.25	0.35	0.18	1.69	0.43	0.18	1.68	
	Avg. 6-7	1.20	0.34	0.20	1.63	0.39	0.17	1.77	0.39
	Composite Test Result, % CO								0.68
IRHC, ppm (C_6)	1	303	276	267	251	251	225	197	
	2	209	169	146	207	142	146	555	
	3	246	182	137	186	133	152	555	
	4	235	179	139	201	126	139	673	
	Avg. 1-4	248	202	172	211	163	167	495	188
	6	234	173	145	195	134	147	701	
	7	235	177	125	185	118	134	615	
	Avg. 6-7	235	176	136	191	127	141	659	167
	Composite Test Result, ppm HC								174
NO, ppm	1	243	303	127	149	166	986	359	
	2	471	1052	717	227	233	1509	363	
	3	153	942	766	249	255	1577	400	
	4	176	1057	703	218	219	1581	405	
	Avg. 1-4	261	839	579	211	219	1414	382	959
	6	188	1091	692	202	189	1568	424	
	7	175	1065	608	209	169	1537	429	
	Avg. 6-7	182	1079	650	206	179	1553	427	1086
	Composite Test Result, ppm NO								1041

TABLE B-15

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 72

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.51	5.57	6.85	5.75	5.86	2.86	3.18	
	2	.90	.38	.28	3.48	1.28	.27	3.15	
	3	2.47	.69	.20	2.77	.76	.27	2.45	
	4	2.10	.64	.22	2.23	.78	.25	2.47	
	Avg. 1-4	2.75	1.82	1.89	3.56	2.17	.91	2.81	1.58
	6	1.94	.58	.22	2.29	1.07	.27	2.54	
	7	2.04	.58	.27	2.17	.89	.26	2.56	
	Avg. 6-7	1.99	.59	.25	2.23	.98	.27	2.55	.61
	Composite Test Result, % CO								.95
IRHC, ppm (C_6)	1	324	297	293	273	271	233	190	
	2	212	165	130	221	155	145	493	
	3	267	176	127	209	132	135	458	
	4	258	173	126	196	137	139	491	
	Avg. 1-4	265	203	169	225	174	163	408	187
	6	249	171	115	199	131	136	532	
	7	248	164	121	195	133	136	545	
	Avg. 6-7	249	168	118	198	132	136	539	159
	Composite Test Result, ppm HC								168
NO, ppm	1	185	196	78	89	89	766	342	
	2	448	1072	815	232	181	1484	345	
	3	116	1069	779	253	239	1623	374	
	4	142	1091	755	243	199	1511	403	
	Avg. 1-4	223	857	607	205	177	1346	367	931
	6	155	1055	630	230	162	1745	455	
	7	151	1010	593	219	145	1449	417	
	Avg. 6-7	154	1033	612	225	154	1463	437	1029
	Composite Test Result, ppm NO								994

TABLE B-16

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 73

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	7.98	4.32	2.43	5.14	3.54	1.71	6.33	
	2	3.82	2.33	.97	4.19	3.66	1.24	5.19	
	3	3.37	1.50	.35	3.09	3.40	.44	3.88	
	4	2.71	1.02	.56	2.85	3.61	.53	3.94	
	Avg. 1-4	4.47	2.29	1.08	3.82	3.55	.98	4.84	1.84
	6	3.02	1.27	.95	2.96	3.98	.65	3.74	
	7	2.91	1.11	.76	3.08	3.68	.56	3.69	
	Avg. 6-7	2.97	1.19	.86	3.02	3.83	.61	3.72	1.27
	Composite Test Result, % CO								1.46
IRHC, ppm (C_6)	1	687	471	367	837	473	353	1420	
	2	453	431	368	419	487	349	1207	
	3	367	355	306	459	448	301	1413	
	4	321	302	295	614	439	290	1563	
	Avg. 1-4	457	390	614	439	462	324	1401	399
	6	493	341	281	806	504	298	1637	
	7	326	310	325	504	427	283	1637	
	Avg. 6-7	410	326	303	826	467	291	1637	385
	Composite Test Result, ppm HC								389
NO, ppm	1	55	879	1161	413	425	1903	215	
	2	86	1306	1713	513	351	2344	321	
	3	113	1789	2097	599	419	3044	526	
	4	121	2011	1708	525	345	2957	619	
	Avg. 1-4	95	1528	1670	512	385	2563	421	1793
	6	93	1788	1213	433	191	2811	578	
	7	92	1899	1377	465	199	2863	570	
	Avg. 6-7	93	1845	1295	449	195	2838	575	1950
	Composite Test Result, ppm NO								1894

TABLE B-17

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 74

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	.72	2.59	2.11	2.35	1.40	2.10	2.21	
	2	.89	.73	.19	.50	.27	.63	.59	
	3	.38	.54	.17	.30	.16	.54	.50	
	4	.33	.62	.16	.34	.26	.60	.56	
	Avg. 1-4	.58	1.12	.66	.87	.52	.97	.97	.90
	6	.48	.67	.19	.47	.27	.65	.67	
	7	.51	.66	.18	.45	.28	.65	.73	
	Avg. 6-7	.50	.67	.19	.46	.28	.65	.70	.53
	Composite Test Result, % CO								.65
IRHC, ppm (C_6)	1	421	250	250	219	124	157	317	
	2	141	105	155	147	72	106	505	
	3	107	97	143	175	59	92	485	
	4	93	86	131	127	54	89	449	
	Avg. 1-4	191	134	170	167	77	111	439	135
	6	85	75	165	154	53	89	477	
	7	88	75	133	109	42	83	450	
	Avg. 6-7	87	75	150	132	49	86	464	101
	Composite Test Result, ppm HC								112
NO, ppm	1	134	371	761	296	177	1046	373	
	2	141	577	1041	440	203	1025	568	
	3	186	647	1203	523	222	1085	569	
	4	210	668	1271	552	213	1139	565	
	Avg. 1-4	169	566	1070	453	204	1074	519	765
	6	207	613	1279	535	197	1075	605	
	7	206	625	1403	573	196	1109	623	
	Avg. 6-7	207	619	1342	554	197	1093	615	875
	Composite Test Result, ppm NO								836

TABLE B-18

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 75

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	1.78	3.12	3.38	2.49	1.32	2.51	2.67	
	2	.92	.56	.14	.46	.18	.40	.47	
	3	.47	.38	.12	.26	.19	.37	.47	
	4	.35	.67	.14	.24	.14	.38	.52	
	Avg. 1-4	.88	1.12	.95	.86	.46	.92	1.03	.92
	6	.48	.44	.14	.32	.25	.48	.57	
	7	.47	.40	.14	.34	.27	.32	.55	
	Avg. 6-7	.48	.42	.14	.33	.26	.40	.56	.34
	Composite Test Result, % CO								.54
IRHC, ppm (C_6)	1	543	339	294	242	112	176	324	
	2	145	99	148	150	54	95	353	
	3	92	74	133	167	55	85	433	
	4	82	70	126	110	38	80	359	
	Avg. 1-4	216	146	175	168	65	109	367	136
	6	86	74	130	149	55	96	416	
	7	81	64	127	126	37	74	458	
	Avg. 6-7	84	70	129	138	47	85	437	96
	Composite Test Result, ppm HC								110
NO, ppm	1	425	596	678	303	193	665	451	
	2	166	754	1699	624	264	1313	675	
	3	218	823	1768	744	246	1448	743	
	4	242	818	1552	671	249	1502	730	
	Avg. 1-4	263	748	1425	586	238	1232	650	986
	6	245	711	1605	699	210	1499	727	
	7	241	707	1661	664	234	1427	728	
	Avg. 6-7	244	710	1633	682	222	1464	728	1116
	Composite Test Result, ppm NO								1070

TABLE B-19

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 76

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.04	3.21	2.20	5.46	3.61	1.78	6.65	
	2	4.26	2.41	1.26	4.52	3.80	1.31	5.42	
	3	3.56	1.78	.34	3.28	3.30	.34	3.75	
	4	2.88	1.17	.47	2.84	3.55	.39	3.80	
	Avg. 1-4	4.18	2.15	1.07	4.02	3.56	.95	4.91	1.81
	6	3.12	1.21	.81	3.02	3.87	.42	3.81	
	7	3.11	1.17	.87	3.02	3.90	.51	3.79	
	Avg. 6-7	3.12	1.19	.84	3.02	3.89	.47	3.80	1.20
	Composite Test Result, % CO								1.41
IRHC, ppm (C_6)	1	579	431	431	956	499	367	1583	
	2	515	470	432	518	499	363	1389	
	3	414	386	355	395	449	321	1616	
	4	369	341	351	717	451	299	1693	
	Avg. 1-4	469	408	393	647	475	338	1571	425
	6	357	321	335	793	428	287	1785	
	7	381	327	335	848	435	297	1779	
	Avg. 6-7	369	325	336	821	432	292	1782	390
	Composite Test Result, ppm HC								401
NO, ppm	1	232	1266	1429	444	478	2035	187	
	2	95	1467	1777	482	437	2533	287	
	3	125	1846	2228	599	487	3226	574	
	4	133	2093	2076	617	392	3379	559	
	Avg. 1-4	147	1668	1878	536	449	2793	401	1970
	6	100	1987	1563	499	190	3177	588	
	7	94	2026	1507	483	190	2975	571	
	Avg. 6-7	97	2007	1536	492	191	3077	580	2128
	Composite Test Result, ppm NO								2073

TABLE B-20

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 77

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

	Mode No.	1	2	3	4	5	6	7	Corr. & Wtd.
	Wtg. Factors	0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	7.11	4.18	2.72	5.57	3.48	1.47	6.88	
	2	4.03	2.40	1.25	4.77	3.55	1.28	5.77	
	3	3.24	1.58	.40	3.23	3.07	.40	4.01	
	4	2.44	.94	.39	2.46	3.05	.38	3.72	
	Avg. 1-4	4.21	2.27	1.20	4.01	3.29	.88	5.10	1.81
	6	2.59	1.15	.52	2.63	3.48	.47	3.57	
	7	2.52	1.13	.59	2.67	3.41	.40	3.57	
	Avg. 6-7	2.56	1.14	.56	2.65	3.45	.44	3.57	1.07
	Composite Test Result, % CO								1.32
IRHC, ppm (C_6)	1	974	620	438	961	486	393	1499	
	2	455	438	440	535	465	368	1358	
	3	392	381	357	377	406	328	1573	
	4	379	348	317	622	387	307	1551	
	Avg. 1-4	550	447	388	624	437	349	1496	437
	6	393	335	323	756	405	297	1620	
	7	385	[illegible]	317	805	446	297	1811	
	Avg. 6-7	390	333	321	781	426	298	1716	387
	Composite Test Result, ppm HC								404
NO, ppm	1	165	1022	1251	422	444	2254	171	
	2	86	1411	1775	494	411	2549	299	
	3	125	1863	2266	585	483	3172	511	
	4	126	2197	1971	623	363	3294	512	
	Avg. 1-4	126	1623	1816	531	425	2817	373	1959
	6	101	1961	1662	539	285	3133	577	
	7	91	1877	1439	491	238	3159	578	
	Avg. 6-7	97	1919	1551	515	261	3147	578	2146
	Composite Test Result, ppm NO								2081

TABLE B-21

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 78

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

	Mode No.	1	2	3	4	5	6	7	Corr. & Wtd.
	Wtg. Factors	0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.15	4.89	6.35	5.36	5.28	2.14	2.83	
	2	.90	.34	.21	3.31	.84	.20	2.84	
	3	2.01	.53	.21	2.39	1.05	.23	2.43	
	4	1.79	.50	.18	1.85	.72	.23	2.32	
	Avg. 1-4	2.47	1.57	1.74	3.23	1.97	.70	2.61	1.36
	6	1.69	.41	.22	1.99	.71	.21	2.41	
	7	1.68	.47	.23	2.02	.62	.21	2.38	
	Avg. 6-7	1.69	.44	.23	2.01	.67	.21	2.40	.51
	Composite Test Result, % CO								.80
IRHC, ppm (C_6)	1	296	266	260	249	240	209	160	
	2	194	150	125	197	129	139	387	
	3	235	160	108	167	117	126	493	
	4	225	151	104	165	112	125	543	
	Avg. 1-4	237	182	149	195	150	150	396	169
	6	230	154	116	159	112	126	569	
	7	222	153	125	170	103	123	569	
	Avg. 6-7	227	154	121	165	108	125	569	148
	Composite Test Result, ppm HC								154
NO, ppm	1	273	344	127	149	149	1164	383	
	2	507	1210	871	256	219	1651	387	
	3	165	1141	832	275	188	1774	448	
	4	182	1205	784	252	219	1654	446	
	Avg. 1-4	281	975	654	233	194	1561	417	1071
	6	193	1243	787	255	176	1707	486	
	7	191	1155	691	221	215	1705	508	
	Avg. 6-7	193	1200	739	239	196	1707	497	1201
	Composite Test Result, ppm NO								1155

TABLE B-22

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 79

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	4.92	4.95	6.13	5.07	4.95	1.98	3.05	
	2	.98	.35	.24	2.70	.44	.19	2.58	
	3	1.44	.47	.21	1.89	.30	.22	1.91	
	4	1.26	.42	.21	1.62	.32	.23	1.63	
	Avg. 1-4	2.15	1.55	1.70	2.82	1.51	.66	2.29	1.25
	6	1.05	.32	.20	1.43	.38	.21	1.74	
	7	1.06	.33	.20	1.42	.38	.22	1.81	
	Avg. 6-7	1.06	.33	.20	1.43	.38	.22	1.78	.39
	Composite Test Result, % CO								.68
IRHC, ppm (C_6)	1	276	257	231	230	219	198	249	
	2	203	166	126	213	131	132	515	
	3	320	187	119	189	106	124	642	
	4	225	162	122	181	119	125	709	
	Avg. 1-4	257	193	150	203	144	145	529	174
	6	203	154	114	179	133	129	727	
	7	205	156	127	180	105	125	797	
	Avg. 6-7	205	156	121	180	119	127	763	156
	Composite Test Result, ppm HC								162
NO, ppm	1	258	291	110	140	153	1103	321	
	2	389	1028	752	232	233	1516	350	
	3	159	971	766	249	253	1537	401	
	4	165	1055	802	245	197	1553	417	
	Avg. 1-4	243	837	607	216	209	1427	372	967
	6	186	993	1023	248	203	1532	471	
	7	181	1023	636	215	192	1428	486	
	Avg. 6-7	183	1009	659	232	198	1480	479	1041
	Composite Test Result, ppm NO								1014

TABLE B-23

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 80

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.10	3.13	1.80	5.04	3.11	1.31	6.57	
	2	4.14	2.33	1.17	4.57	3.72	1.18	5.77	
	3	3.61	1.52	0.28	3.16	3.24	0.40	4.08	
	4	2.86	1.18	0.51	2.98	3.47	0.46	3.93	
	Avg. 1-4	4.18	2.04	0.94	3.94	3.39	0.84	5.09	1.70
	6	3.17	1.35	0.87	3.02	3.71	0.49	3.93	
	7	3.09	1.26	0.77	2.93	3.66	0.47	3.82	
	Avg. 6-7	3.13	1.31	0.83	2.98	3.69	0.48	3.88	1.23
	Composite Test Result, % CO								1.39
IRHC, ppm (C_6)	1	610	450	378	844	455	344	1465	
	2	400	377	348	464	448	326	1377	
	3	348	340	330	440	398	302	1587	
	4	320	325	337	566	421	292	1644	
	Avg. 1-4	420	374	349	579	431	316	1518	392
	6	333	316	445	736	428	290	1790	
	7	335	324	335	827	457	297	1838	
	Avg. 6-7	335	321	338	782	444	294	1814	387
	Composite Test Result, ppm HC								388
NO, ppm	1	217	1157	1361	431	454	2057	173	
	2	83	1317	1722	473	396	2382	271	
	3	100	1735	2158	582	417	2810	549	
	4	112	1792	1908	516	344	2771	511	
	Avg. 1-4	128	1501	1787	501	403	2505	377	1782
	6	85	1650	1249	396	238	2725	582	
	7	83	1731	1225	403	207	2710	493	
	Avg. 6-7	84	1691	1238	400	223	2718	538	1847
	Composite Test Result, ppm NO								1824

TABLE B-24

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 81

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.91	3.32	1.87	5.42	2.72	1.05	6.87	
	2	4.13	1.94	1.07	5.00	3.90	.98	6.39	
	3	3.63	1.51	.36	3.38	3.17	.38	4.98	
	4	3.00	1.24	.59	3.26	3.45	.46	4.64	
	Avg. 1-4	4.17	2.00	.97	4.27	3.31	.72	5.72	1.68
	6	3.24	1.42	.62	3.12	3.70	.50	4.32	
	7	3.25	1.40	.78	3.11	3.64	.53	4.22	
	Avg. 6-7	3.24	1.41	.70	3.12	3.67	.52	4.27	1.28
	Composite Test Result, % CO								1.41
IRHC, ppm (C_6)	1	620	450	553	990	573	326	1272	
	2	321	309	313	462	337	268	1183	
	3	292	290	260	302	310	255	1192	
	4	264	261	236	343	302	240	1376	
	Avg. 1-4	374	328	340	524	380	273	1256	345
	6	271	267	248	518	313	241	1465	
	7	272	262	264	554	316	240	1460	
	Avg. 6-7	272	265	257	537	315	241	1464	306
	Composite Test Result, ppm HC								319
NO, ppm	1	331	1174	1592	532	667	2382	187	
	2	96	1587	2052	555	455	2625	297	
	3	133	1833	2232	617	479	2916	431	
	4	134	1802	1952	567	462	2858	501	
	Avg. 1-4	174	1600	1957	568	516	2696	354	1923
	6	107	1699	1608	528	248	2880	514	
	7	95	1714	1550	479	213	2780	482	
	Avg. 6-7	102	1707	1580	504	231	2830	498	1950
	Composite Test Result, ppm NO								1940

TABLE B-25

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 77B

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.36	3.64	2.42	5.54	3.10	1.62	6.79	
	2	3.82	2.08	1.04	4.24	3.40	1.19	5.34	
	3	3.12	1.20	.24	2.58	2.68	.36	3.80	
	4	2.67	1.02	.51	2.86	3.20	.42	3.96	
	Avg. 1-4	3.99	1.98	1.05	3.81	3.10	.90	4.98	1.69
	6	2.77	1.10	.58	2.86	3.57	.64	3.78	
	7	2.79	1.10	.62	2.82	3.41	.44	3.75	
	Avg. 6-7	2.78	1.11	.60	2.84	3.50	.54	3.77	1.13
	Composite Test Result, % CO								1.32
IRHC, ppm (C_6)	1	684	494	610	942	590	450	1428	
	2	419	466	552	452	530	404	1238	
	3	355	376	388	492	453	316	1443	
	4	316	315	319	487	494	278	1561	
	Avg. 1-4	444	413	480	594	517	362	1418	442
	6	320	304	286	584	396	266	1667	
	7	317	292	286	642	369	254	1654	
	Avg. 6-7	319	299	287	613	383	260	1661	342
	Composite Test Result, ppm HC								376
NO, ppm	1	209	1092	1406	482	592	2241	175	
	2	104	1587	2011	604	500	2624	334	
	3	145	1981	2270	664	707	3333	522	
	4	131	2070	2223	628	399	3274	556	
	Avg. 1-4	147	1682	1978	594	550	2868	396	2029
	6	100	1961	1630	546	315	2886	574	
	7	97	1899	1502	527	253	3048	573	
	Avg. 6-7	99	1931	1566	537	284	2967	574	2072
	Composite Test Result, ppm NO								2057

TABLE B-26

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 82

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.78	5.64	6.92	5.69	5.72	3.27	3.53	
	2	.83	.31	.35	3.68	.78	.21	3.12	
	3	1.91	.51	.20	2.26	.52	.22	2.21	
	4	1.64	.47	.21	1.89	.60	.24	2.25	
	Avg. 1-4	2.54	1.74	1.92	3.38	1.90	.99	2.78	1.56
	6	1.55	.42	.18	1.81	.45	.23	2.04	
	7	1.46	.41	.17	1.82	.44	.22	2.11	
	Avg. 6-7	1.51	.42	.18	1.82	.45	.23	2.08	.45
	Composite Test Result, % CO								.83
IRHC, ppm (C_6)	1	316	291	283	274	267	241	195	
	2	205	168	139	207	135	149	431	
	3	238	171	129	169	123	140	495	
	4	222	154	123	181	112	136	539	
	Avg. 1-4	245	197	169	208	159	167	415	183
	6	217	149	107	171	105	126	572	
	7	217	229	121	167	116	133	598	
	Avg. 6-7	217	153	114	169	111	130	585	150
	Composite Test Result, ppm HC								161
NO, ppm	1	196	245	103	121	127	705	356	
	2	472	1199	938	283	249	1593	385	
	3	172	1119	829	283	261	1671	413	
	4	197	1175	880	273	217	1701	434	
	Avg. 1-4	259	935	687	241	214	1418	397	999
	6	203	1075	761	261	218	1604	464	
	7	206	1109	784	280	246	1558	483	
	Avg. 6-7	205	1092	773	271	233	1581	474	1126
	Composite Test Result, ppm NO								1081

TABLE B-27

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 83

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	1.60	4.24	3.86	2.48	1.72	2.38	1.15	
	2	.79	.68	.14	.40	.11	.42	.42	
	3	.20	.53	.11	.16	.11	.42	.34	
	4	.17	.47	.11	.16	.12	.40	.35	
	Avg. 1-4	.69	1.48	1.06	.80	.52	.91	.56	1.00
	6	.24	.45	.13	.22	.08	.40	.42	
	7	.24	.42	.13	.22	.08	.37	.44	
	Avg. 6-7	.25	.44	.13	.22	.08	.38	.43	.32
	Composite Test Result, % CO								.54
IRHC, ppm (C_6)	1	222	239	368	277	140	200	691	
	2	155	122	227	223	64	120	808	
	3	127	100	164	182	57	105	821	
	4	120	96	178	208	59	120	788	
	Avg. 1-4	156	140	234	222	80	136	777	168
	6	105	82	165	146	42	105	778	
	7	106	82	170	178	46	110	782	
	Avg. 6-7	106	83	168	162	44	108	781	126
	Composite Test Result, ppm HC								140
NO, ppm	1	111	214	652	404	227	724	594	
	2	182	685	1188	598	256	1303	746	
	3	281	803	1416	650	248	1410	837	
	4	290	766	1500	711	244	1531	803	
	Avg. 1-4	216	618	1190	591	244	1242	746	933
	6	278	748	1715	727	241	1497	808	
	7	279	710	1688	753	240	1469	782	
	Avg. 6-7	280	729	1702	741	241	1483	796	1144
	Composite Test Result, ppm NO								1070

TABLE B-28

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 84

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.89	4.30	5.02	3.39	2.74	2.56	2.33	
	2	.74	.62	.14	.32	.20	.31	.34	
	3	.16	.40	.12	.16	.10	.30	.28	
	4	.26	.42	.12	.20	.10	.38	.36	
	Avg. 1-4	1.01	1.44	1.35	1.02	.78	.89	.83	1.05
	6	.26	.42	.12	.22	.08	.26	.36	
	7	.26	.43	.12	.24	.09	.36	.40	
	Avg. 6-7	.26	.43	.12	.24	.08	.32	.38	.28
	Composite Test Result, % CO								.54
IRHC, ppm (C_6)	1	221	194	280	212	113	145	312	
	2	96	80	137	152	42	73	556	
	3	72	56	104	130	26	60	481	
	4	63	54	110	144	22	66	556	
	Avg. 1-4	113	96	158	160	52	87	476	110
	6	63	46	141	148	22	64	732	
	7	58	43	132	151	18	67	713	
	Avg. 6-7	61	45	136	150	20	66	723	89
	Composite Test Result, ppm HC								96
NO, ppm	1	79	204	433	222	206	655	439	
	2	192	786	1516	601	268	1295	762	
	3	298	803	1583	690	272	1318	750	
	4	287	750	1516	658	262	1468	756	
	Avg. 1-4	214	636	1262	543	252	1185	676	915
	6	282	668	1689	682	260	1189	792	
	7	281	635	1529	640	242	1381	776	
	Avg. 6-7	282	652	1610	662	251	1436	784	1088
	Composite Test Result, ppm NO								1027

Very rich idle in start of Block 1 from repeated attempts to set choke, causing fuel in manifold.

TABLE B-29

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 85

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.26	2.68	2.12	5.52	3.39	1.34	6.86	
	2	3.80	2.18	1.09	4.50	3.29	1.16	5.56	
	3	3.13	1.26	.18	2.65	2.80	.32	4.16	
	4	2.48	1.06	.51	2.78	3.28	.37	3.99	
	Avg. 1-4	3.92	1.80	.98	3.86	3.19	.80	5.14	1.60
	6	2.72	1.02	.48	2.86	3.46	.42	3.93	
	7	2.54	1.00	.62	2.66	3.26	.44	3.90	
	Avg. 6-7	2.63	1.02	.55	2.76	3.36	.43	3.92	1.06
	Composite Test Result, % CO								1.24
IRHC, ppm (C_6)	1	531	377	474	913	461	407	1531	
	2	412	396	393	421	384	372	1308	
	3	335	365	427	503	462	314	1510	
	4	295	319	273	474	395	290	1556	
	Avg. 1-4	394	365	392	578	426	346	1476	406
	6	293	263	281	635	352	233	1725	
	7	287	265	267	631	328	224	1752	
	Avg. 6-7	291	265	275	633	340	229	1739	318
	Composite Test Result, ppm HC								348
NO, ppm	1	236	1371	1335	461	528	2248	167	
	2	113	1520	1824	513	595	2523	300	
	3	169	1929	2368	660	551	3136	490	
	4	148	2053	1935	534	426	3212	523	
	Avg. 1-4	166	1719	1866	543	559	2780	370	1929
	6	113	1986	1715	527	291	3060	544	
	7	104	1898	1566	481	278	2935	548	
	Avg. 6-7	109	1943	1641	504	286	2998	546	2096
	Composite Test Result, ppm NO								2055

TABLE B-30

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 86

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.41	5.48	6.14	4.84	4.58	1.97	3.02	
	2	.81	.32	.33	2.38	.37	.16	2.30	
	3	1.14	.38	.17	1.56	.44	.17	1.71	
	4	1.16	.35	.16	1.45	.33	.19	1.61	
	Avg. 1-4	2.14	1.64	1.70	2.56	1.43	.62	2.16	1.24
	6	1.01	.30	.16	1.41	.41	.18	1.68	
	7	1.09	.34	.18	1.50	.38	.19	1.90	
	Avg. 6-7	1.05	.32	.18	1.46	.40	.19	1.80	.37
	Composite Test Result, % CO								.67
IRHC, ppm (C_6)	1	211	200	173	165	160	142	208	
	2	157	118	98	138	83	97	489	
	3	165	117	86	120	82	88	510	
	4	166	120	86	124	79	88	579	
	Avg. 1-4	174	139	111	137	102	104	446	126
	6	162	122	82	116	79	88	607	
	7	164	121	86	127	80	96	666	
	Avg. 6-7	164	122	84	122	80	92	637	116
	Composite Test Result, ppm HC								118
NO, ppm	1	164	174	102	123	138	860	296	
	2	411	1055	770	250	211	1521	378	
	3	186	1025	749	236	194	1690	381	
	4	202	1104	696	246	204	1640	414	
	Avg. 1-4	240	840	580	214	187	1427	367	964
	6	198	1066	678	244	178	1616	457	
	7	204	1048	652	226	164	1568	473	
	Avg. 6-7	201	1058	665	235	172	1593	465	1104
	Composite Test Result, ppm NO								1055

TABLE B-31

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 87

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	.55	3.00	3.24	2.93	1.53	3.29	2.05	
	2	.74	.63	.19	.35	.22	.42	.35	
	3	.14	.38	.15	.18	.29	.35	.35	
	4	.16	.46	.15	.21	.20	.37	.38	
	Avg. 1-4	.40	1.12	.94	.92	.56	1.11	.78	.98
	6	.18	.44	.14	.26	.14	.40	.49	
	7	.25	.44	.14	.27	.14	.42	.52	
	Avg. 6-7	.22	.44	.14	.26	.14	.42	.50	.34
	Composite Test Result, % CO								.56
IRHC, ppm (C_6)	1	348	165	198	166	79	122	312	
	2	85	62	106	112	30	59	236	
	3	56	46	125	111	29	52	348	
	4	52	46	114	94	22	52	390	
	Avg. 1-4	135	80	136	121	40	72	322	90
	6	52	35	86	112	22	56	468	
	7	52	42	112	96	22	56	416	
	Avg. 6-7	52	39	100	104	22	56	442	68
	Composite Test Result, ppm HC								75
NO, ppm	1	146	344	931	316	205	539	491	
	2	180	771	1320	572	231	1407	813	
	3	237	913	1428	600	248	1588	735	
	4	250	868	1522	552	227	1579	712	
	Avg. 1-4	204	724	1300	510	228	1278	688	981
	6	252	764	1520	612	233	1508	665	
	7	245	796	1511	593	228	1561	696	
	Avg. 6-7	249	780	1516	603	231	1535	681	1145
	Composite Test Result, ppm NO								1087

TABLE B-32

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 88

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	3.08	4.65	3.55	3.03	1.66	3.30	2.42	
	2	.72	.54	.12	.32	.16	.40	.42	
	3	.12	.46	.12	.17	.22	.34	.36	
	4	.11	.38	.12	.18	.10	.34	.34	
	Avg. 1-4	1.00	1.50	.98	.93	.54	1.10	.88	1.11
	6	.16	.42	.12	.22	.11	.28	.40	
	7	.20	.44	.13	.22	.11	.38	.47	
	Avg. 6-7	.18	.44	.13	.22	.12	.34	.44	.28
	Composite Test Result, % CO								.56
IRHC, ppm (C_6)	1	297	227	220	179	83	129	300	
	2	81	63	116	121	30	64	440	
	3	73	59	130	[illegible]	54	64	531	
	4	54	38	93	113	17	48	569	
	Avg. 1-4	126	97	140	144	46	77	460	102
	6	41	38	104	118	16	43	521	
	7	53	44	91	92	16	53	571	
	Avg. 6-7	47	41	98	106	16	49	546	66
	Composite Test Result, ppm HC								78
NO, ppm	1	179	326	652	262	205	517	413	
	2	191	704	1342	539	252	1396	630	
	3	233	906	1443	556	252	1494	624	
	4	233	873	1362	534	233	1353	657	
	Avg. 1-4	209	702	1200	473	236	1190	582	918
	6	222	841	1360	552	211	1356	685	
	7	227	794	1416	538	215	1439	661	
	Avg. 6-7	225	818	1389	546	213	1398	674	1072
	Composite Test Result, ppm NO								1018

TABLE B-33

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 89

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.72	3.95	1.98	5.38	3.35	1.06	6.53	
	2	3.59	2.02	.90	4.14	3.40	.98	5.38	
	3	3.08	1.32	.27	2.75	2.84	.40	4.20	
	4	2.65	1.06	.43	2.81	3.27	.47	4.28	
	Avg. 1-4	4.02	2.09	.89	3.77	3.22	.73	5.10	1.62
	6	2.92	1.02	.94	3.06	3.75	.65	4.06	
	7	2.84	1.11	.54	3.07	3.59	.46	4.12	
	Avg. 6-7	2.88	1.07	.74	3.06	3.68	.56	4.09	1.20
	Composite Test Result, % CO								1.34
IRHC, ppm (C_6)	1	869	650	356	762	366	268	1408	
	2	309	300	256	312	300	236	1202	
	3	264	260	231	273	257	210	1266	
	4	229	227	222	328	264	190	1319	
	Avg. 1-4	418	360	266	419	292	226	1299	316
	6	228	216	206	405	274	192	1504	
	7	222	212	222	496	260	184	1518	
	Avg. 6-7	225	215	214	452	267	188	1512	256
	Composite Test Result, ppm HC								276
NO, ppm	1	280	1060	1339	447	508	2320	203	
	2	104	1473	1809	550	486	2595	318	
	3	140	1854	1928	578	520	2964	498	
	4	148	1960	1833	540	333	2998	503	
	Avg. 1-4	168	1587	1728	529	462	2720	380	1900
	6	106	1910	1408	462	259	2646	536	
	7	100	1860	1526	484	254	2786	556	
	Avg. 6-7	103	1886	1468	464	257	2717	548	1928
	Composite Test Result, ppm NO								1918

High CO (14%) and HC, with misfire, in start-up idle of Block 2, then normal.

TABLE B-34

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 89B

Data are averages from first 7 cycles of 2 12-cycle blocks. (See Note)

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	8.22	5.92	2.20	5.48	3.58	1.40	6.68	
	2	3.59	2.18	.66	4.19	3.38	1.04	5.40	
	3	3.13	1.38	.22	2.80	2.94	.34	4.26	
	4	2.85	1.12	.30	2.92	3.50	.42	4.29	
	Avg. 1-4	4.45	2.65	.84	3.85	3.35	.80	5.16	1.83
	6	3.21	1.23	.97	3.48	3.70	.40	4.40	
	7	3.43	1.36	.74	3.44	3.97	.57	4.34	
	Avg. 6-7	3.32	1.30	.86	3.47	3.84	.48	4.37	1.29
	Composite Test Result, % CO								1.47
IRHC, ppm (C_6)	1	1183	989	387	803	364	299	1182	
	2	289	279	241	313	279	237	1178	
	3	241	235	196	301	242	188	1193	
	4	211	206	168	273	242	174	1300	
	Avg. 1-4	481	428	248	423	282	225	1213	328
	6	216	198	181	351	218	160	1351	
	7	206	186	168	393	238	163	1415	
	Avg. 6-7	212	192	175	372	229	162	1383	223
	Composite Test Result, ppm HC								259
NO, ppm	1	138	546	999	372	344	1761	170	
	2	91	1148	1493	510	362	2094	315	
	3	120	1405	1603	491	430	2392	444	
	4	145	1592	1490	551	365	2520	433	
	Avg. 1-4	123	1173	1397	481	376	2192	341	1510
	6	105	1560	1375	357	167	2588	484	
	7	100	1483	1433	402	157	2384	492	
	Avg. 6-7	103	1522	1404	380	162	2487	488	1716
	Composite Test Result, ppm NO								1644

Note: The cold-start idles of Blocks 1 and 3 had CO estimated about 14%, very high HC, misfire. Relatively high CO, without misfire, persisted to about mode 4. This sheet averages Blocks 2 and 3; no printout was available on Block 1.

TABLE B-35

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 90

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	4.01	5.25	6.24	5.06	4.92	2.08	3.88	
	2	.89	.34	.44	3.60	1.63	.22	4.05	
	3	2.19	.61	.30	2.56	1.00	.22	2.69	
	4	1.82	.50	.21	2.09	.88	.21	2.36	
	Avg. 1-4	2.23	1.68	1.80	3.33	2.11	.68	3.25	1.40
	6	1.61	.44	.24	2.01	.81	.24	2.39	
	7	1.60	.46	.17	1.98	.77	.21	2.21	
	Avg. 6-7	1.60	.45	.21	2.00	.80	.23	2.30	.52
	Composite Test Result, % CO								.83
IRHC, ppm (C_6)	1	222	210	189	184	180	158	174	
	2	144	121	95	138	112	106	373	
	3	168	131	98	124	93	101	232	
	4	158	171	90	116	90	90	295	
	Avg. 1-4	173	146	118	141	119	114	279	129
	6	148	114	82	109	81	90	366	
	7	156	126	95	126	88	98	313	
	Avg. 6-7	153	120	88	118	85	95	340	109
	Composite Test Result, ppm HC								116
NO, ppm	1	604	348	119	170	206	1205	371	
	2	574	1176	919	270	209	1669	398	
	3	161	1159	836	276	212	1821	386	
	4	199	1172	941	300	204	1859	417	
	Avg. 1-4	385	964	704	255	208	1638	393	1114
	6	200	1143	781	264	204	1704	455	
	7	194	1152	800	276	222	1608	473	
	Avg. 6-7	197	1148	791	271	214	1657	464	1174
	Composite Test Result, ppm NO								1153

TABLE B-36

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 91

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	.40	2.45	2.58	2.20	1.53	3.23	1.61	
	2	.97	.63	.14	.70	.52	.63	.25	
	3	.28	.50	.13	.25	.18	.49	.24	
	4	.28	.43	.14	.22	.22	.53	.28	
	Avg. 1-4	.48	1.00	.75	.85	.61	1.22	.60	.98
	6	.42	.55	.14	.34	.30	.48	.35	
	7	.54	.64	.16	.37	.32	.45	.29	
	Avg. 6-7	.48	.60	.16	.36	.31	.46	.32	.42
	Composite Test Result, % CO								.61
IRHC, ppm (C_6)	1	534	289	234	195	122	163	157	
	2	106	86	128	125	70	95	105	
	3	82	66	114	104	56	84	106	
	4	74	64	137	100	53	80	112	
	Avg. 1-4	200	126	154	132	76	106	120	118
	6	82	68	117	95	55	80	107	
	7	76	60	146	121	59	84	110	
	Avg. 6-7	80	64	132	109	57	82	109	82
	Composite Test Result, ppm HC								94
NO, ppm	1	217	692	850	634	191	565	965	
	2	194	780	1763	913	242	1434	1640	
	3	254	854	1675	926	246	1505	1557	
	4	250	808	1601	1022	218	1390	1404	
	Avg. 1-4	229	784	1472	874	224	1224	1392	1035
	6	238	713	1652	934	213	1400	1276	
	7	236	670	1455	812	207	1404	1457	
	Avg. 6-7	237	692	1554	874	210	1402	1367	1102
	Composite Test Result, ppm NO								1078

TABLE B-37

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 92

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.28	5.54	7.00	6.00	5.92	2.98	3.42	
	2	.86	.29	.16	3.28	.72	.14	3.08	
	3	1.98	.52	.18	2.24	.70	.17	2.35	
	4	1.64	.43	.14	1.84	.65	.18	2.10	
	Avg. 1-4	2.44	1.70	1.88	3.36	2.00	.87	2.74	1.50
	6	1.26	.42	.15	1.86	.70	.18	2.15	
	7	1.41	.43	.15	1.72	.44	.20	2.40	
	Avg. 6-7	1.34	.43	.16	1.80	.58	.20	2.28	.46
	Composite Test Result, % CO								.81
IRHC, ppm (C_6)	1	160	148	146	142	134	118	100	
	2	97	77	64	110	67	69	275	
	3	126	88	58	93	61	62	260	
	4	117	77	57	85	52	62	350	
	Avg. 1-4	125	98	82	108	79	78	246	90
	6	114	84	64	95	56	69	348	
	7	118	84	52	85	52	56	432	
	Avg. 6-7	116	84	58	90	55	59	391	76
	Composite Test Result, ppm HC								80
NO, ppm	1	290	263	84	108	117	844	408	
	2	563	1245	1119	321	322	1734	384	
	3	182	1100	1052	320	259	1821	414	
	4	225	1209	957	344	276	1849	471	
	Avg. 1-4	316	955	803	274	243	1563	419	1090
	6	250	1123	884	284	255	1770	462	
	7	231	1162	798	292	264	1750	522	
	Avg. 6-7	241	1143	842	288	260	1760	492	1233
	Composite Test Result, ppm NO								1182

TABLE B-38

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 93

Data are averages from first 7 cycles of 1 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	7.62	4.96	3.66	5.68	3.41	2.50	6.72	
	2	3.76	3.12	2.46	4.58	3.64	2.67	5.69	
	3	3.18	1.95	.92	3.09	3.01	.66	4.14	
	4	2.36	1.35	.61	2.48	3.03	.96	3.90	
	Avg. 1-4	4.23	2.84	1.91	3.96	3.27	1.70	5.11	2.40
	6	2.45	1.57	.86	2.50	3.08	1.10	3.66	
	7	2.32	1.40	.99	2.42	3.12	1.09	3.43	
	Avg. 6-7	2.38	1.49	.93	2.46	3.10	1.10	3.55	1.46
	Composite Test Result, % CO								1.78
IRHC, ppm (C_6)	1	521	326	248	962	314	254	1721	
	2	510	390	308	506	353	294	1321	
	3	390	298	239	322	292	222	1679	
	4	303	249	216	658	280	206	1764	
	Avg. 1-4	432	316	253	612	310	243	1622	334
	6	312	244	208	800	292	198	1785	
	7	316	238	204	831	288	199	1851	
	Avg. 6-7	314	241	206	816	290	199	1818	303
	Composite Test Result, ppm HC								313
NO, ppm	1	75	519	530	221	269	1168	116	
	2	217	895	775	275	318	1216	200	
	3	306	1246	1261	368	289	2028	358	
	4	98	1285	1196	438	291	1829	365	
	Avg. 1-4	175	986	941	326	292	1560	260	1108
	6	100	1214	900	366	256	1701	372	
	7	100	1194	800	327	231	1644	418	
	Avg. 6-7	100	1204	850	346	243	1673	396	1202
	Composite Test Result, ppm NO								1170

TABLE B-39

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 94

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.92	3.98	5.26	3.88	3.51	1.03	4.12	
	2	.97	.36	.19	3.84	.90	.16	3.92	
	3	2.23	.62	.19	2.76	.84	.20	2.58	
	4	1.81	.58	.16	2.02	.65	.22	2.26	
	Avg. 1-4	1.98	1.38	1.43	3.12	1.48	.40	3.22	1.11
	6	1.53	.43	.14	1.88	.58	.20	2.23	
	7	1.56	.47	.14	1.96	.68	.22	2.26	
	Avg. 6-7	1.55	.45	.14	1.92	.63	.21	2.25	.48
	Composite Test Result, % CO								.69
IRHC, ppm (C_6)	1	236	223	214	201	201	186	208	
	2	186	157	132	194	140	144	370	
	3	214	168	124	170	124	128	333	
	4	196	159	115	158	116	124	412	
	Avg. 1-4	208	178	147	180	146	146	331	160
	6	194	151	114	152	108	124	408	
	7	198	152	114	151	112	120	409	
	Avg. 6-7	197	152	114	152	110	123	409	138
	Composite Test Result, ppm HC								145
NO, ppm	1	949	598	251	316	356	1707	343	
	2	526	1190	1149	327	285	1742	404	
	3	156	1134	1128	323	264	1830	408	
	4	188	1158	1038	296	248	1844	453	
	Avg. 1-4	455	1020	891	315	288	1781	403	1226
	6	198	1150	982	313	224	1684	452	
	7	200	1208	961	310	224	1795	453	
	Avg. 6-7	200	1179	972	312	224	1740	453	1242
	Composite Test Result, ppm NO								1236

TABLE B-40

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 95

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.72	3.48	2.87	2.43	1.94	2.68	1.13	
	2	.72	.66	.45	.61	.56	.62	.39	
	3	.50	.58	.27	.40	.52	.54	.32	
	4	.64	.64	.32	.43	.56	.55	.48	
	Avg. 1-4	1.15	1.34	.98	.97	.90	1.10	.58	1.09
	6	.74	.62	.32	.52	.54	.52	.51	
	7	.72	.57	.33	.56	.54	.46	.4	
	Avg. 6-7	.73	.60	.33	.54	.54	.49	.46	.50
	Composite Test Result, % CO								.70
IRHC, ppm (C_6)	1	290	242	235	202	122	160	152	
	2	94	86	114	126	63	89	104	
	3	58	59	120	102	46	76	[illegible]	
	4	68	55	102	98	46	76	[illegible]	
	Avg. 1-4	128	110	153	132	69	100	[illegible]	108
	6	70	62	119	100	42	70	250	
	7	63	51	131	115	42	70	102	
	Avg. 6-7	67	57	126	108	42	70	176	76
	Composite Test Result, ppm HC								86
NO, ppm	1	270	394	758	475	170	717	1000	
	2	274	670	1499	1020	240	1132	1610	
	3	342	690	1700	1174	212	1256	1764	
	4	238	689	1575	1088	188	1301	1470	
	Avg. 1-4	281	610	1383	939	202	1102	1462	933
	6	186	586	1544	976	198	1100	1327	
	7	195	633	1374	739	169	1358	1492	
	Avg. 6-7	191	610	1460	858	184	1230	1410	990
	Composite Test Result, ppm NO								970

TABLE B-41

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 96

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.92	5.15	3.60	5.85	3.65	2.23	6.86	
	2	4.16	2.92	1.99	4.63	3.88	2.34	5.65	
	3	3.56	1.62	.50	2.94	3.22	.70	4.25	
	4	2.90	1.50	1.00	2.80	3.38	.92	3.91	
	Avg. 1-4	4.38	2.80	1.78	4.06	3.54	1.55	5.17	2.33
	6	2.84	1.76	1.12	2.84	3.67	1.00	3.83	
	7	2.76	1.58	1.17	2.82	3.48	1.09	3.84	
	Avg. 6-7	2.80	1.66	1.15	2.83	3.58	1.04	3.84	1.58
	Composite Test Result, % CO								1.84
IRHC, ppm (C_6)	1	503	391	292	866	366	309	1472	
	2	500	389	324	500	379	31[illegible]	1224	
	3	416	340	284	554	337	266	1464	
	4	294	284	244	596	310	246	1588	
	Avg. 1-4	428	351	286	629	348	284	1437	362
	6	286	274	230	666	323	238	1691	
	7	294	272	235	740	331	238	1762	
	Avg. 6-7	290	274	233	704	328	239	1727	323
	Composite Test Result, ppm HC								336
NO, ppm	1	129	512	675	230	270	1348	122	
	2	194	959	1012	357	307	1442	258	
	3	300	1386	1403	436	303	2172	424	
	4	99	1350	1026	376	271	1972	398	
	Avg. 1-4	181	1052	1029	350	288	1734	300	1216
	6	86	1114	981	340	170	1913	418	
	7	82	1183	910	300	146	1775	446	
	Avg. 6-7	84	1148	946	321	158	1844	432	1272
	Composite Test Result, ppm NO								1252